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CHEMISTRY:

GENERAL, MEDICAL, AND PHARMACEUTICAL,

INCLUDING

THE CHEMISTRY OF THE U. S. PHARMACOPŒIA.

A MANUAL

ON THE GENERAL PRINCIPLES OF THE SCIENCE, AND THEIR
APPLICATIONS IN MEDICINE AND PHARMACY.

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NEW HAMPSHIRE AND VIRGINIA; PRESIDENT OF THE
BRITISH PHARMACEUTICAL CONFERENCE.

TENTH EDITION,

SPECIALLY REVISED BY THE AUTHOR FOR AMERICA.

PHILADELPHIA:
HENRY C. LEA'S SON & CO.
1883.

92104

"But the greatest error of all is, mistaking the ultimate end of knowledge; for some men covet knowledge out of a natural curiosity and inquisitive temper; some to entertain the mind with variety and delight; some for ornament and reputation; some for victory and contention; many for lucre and a livelihood; and but few for employing the divine gift of reason to the use and benefit of mankind. Thus some appear to seek in knowledge a couch for a searching spirit; others, a walk for a wandering mind; others, a tower of state; others, a fort or commanding ground; and others, a shop for profit or sale; instead of a storehouse for the glory of the Creator and the endowment of human life."—Lord Bacon.

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PREFACE.

THE short title on the back of a book, and even the words on the title-page, are generally, and even necessarily, imperfect descriptions of the contents, and hence not unfrequently induce at the outset misconceptions in the minds of readers. The author of *Chemistry: General, Medical, and Pharmaceutical*, would at once state, therefore, that his chief aim is to teach the general truths of Chemistry to medical and pharmaceutical pupils. So far as laws and principles are concerned, the book is a work on General Chemistry; but, inasmuch as those laws and principles are elucidated and illustrated by that large portion of Chemistry which is directly interesting to medical practitioners and pharmacists, the book may be said to be a work on Medical Chemistry and Pharmaceutical Chemistry. Only in this conventional sense would the author speak of Medical and Pharmaceutical Chemistry, for the truths of Chemistry are the same for all students—crystalline verities which cannot be expanded or compressed to suit any class of workers. The leading principles of the science, however, can as easily be illustrated by or deduced from those facts which have interest as from those which have little or no special interest to the followers of medicine and pharmacy. The grand and simple leading truths of Chemistry, the lesser truths or principles, and nearly all the interesting relationships of elements and compounds—in a word, the *science* of Chemistry—can be taught to medical and pharmaceutical students with little other aid than that afforded by the materials which lie in rich abundance all around these workers. Such a mode of teaching "the general principles of the science, and their applications in medicine and pharmacy," is adopted in this volume. It is a mode which greatly increases the usefulness of the science to the class chiefly addressed, while it in no way diminishes the value of Chemistry as an instrument of mental culture—an instrument which sharpens and expands the powers of observation, which enlarges and strengthens memory and imagination, which gives point to the perceptive faculties, and which develops and elaborates the powers of thought and of reason.

This manual is intended, then, as a systematic exponent of the general truths of Chemistry, but is written mainly for the pupils, assistants, and principals engaged in medicine and pharmacy. It will be found equally useful as a reading-book for gentlemen having no opportunities of attending lectures or performing experiments, or, on the other hand, as a text-book for college pupils; while its comprehensive Index, containing eight thousand references, will fit the work for after-consultation in the course of business or professional practice.

From other chemical text-books it differs in three particulars: first, in the exclusion of matter relating to compounds which at present are only of interest to the scientific chemist; secondly, in containing more or less of the chemistry of every substance recognized officially or in general practice as a remedial agent; thirdly, in the paragraphs being so cast that the volume may be used as a guide in studying the science experimentally.

The order of subjects is that which, in the author's opinion, best meets the requirements of medical and pharmaceutical students in Great Britain, Ireland, America, and the English colonies. Introductory pages are devoted to a few leading properties of the elements. A review of the facts thus unfolded affords opportunity for stating the views of philosophers respecting the manner in which these elements influence each other as components of terrestrial matter. The consideration in detail of the relations of the elementary and compound radicals follows, synthetical and analytical bearings being pointed out, and attention frequently directed to connecting or underlying truths or general principles. The chemistry of substances naturally associated in vegetables and animals is next considered. Practical toxicology, and the chemical as well as microscopical characters of morbid urine, urinary sediments, and calculi, are then given. The concluding sections form a laboratory-guide to the chemical and physical study of quantitative analysis. In the Appendix is a long table of tests for impurities in medicinal preparations; also a short one of the saturating powers of acids and alkalies, designed for use in prescribing and dispensing.

In the course of the treatment outlined in the preceding paragraph it will be observed that the whole of the elements are first noticed very shortly, to give the pupil a general view of his course of study, and afterward at length and thoroughly; that the chemistry of the common metallic radicals precedes that of the rarer, and that the sections on the acidulous radicals are similarly divided; while the basylous radicals are arranged according to analytical relations, the common acidulous according to exchangeable value or quantivalence, and rarer acidulous radicals alphabetically. By this plan the more important facts and principles are repeatedly brought under consideration, the points of view, however, differing according as interest is concentrated on physical, synthetical, analytical, or quantitative properties. This arrangement of matter was adopted, also, partly from the belief that the separate and general truths of Chemistry never enter the mind in the order of any scientific classification at present possible. In the current state of chemical knowledge consistency in the methodical arrangement even of elements can only be carried out in one direction, and is necessarily accompanied by inconsistencies in other directions—a result most perplexing to learners, and hence totally subversive of the chief advantage of classification. For this reason the writer has preferred to lead up to, rather than follow, scientific classification—has allowed analogies and affinities to suggest, rather than be suggested by, classification. Among the acidulous radicals, especially, any known system of classification would have given undue prominence to one set of relations and undeserved obscurity to others. Then, by separating more important from less important matter, instruction is adapted to the wants of gentlemen whose opportunities of studying Chemistry vary greatly, and are unavoidably insufficient to enable them to gain a knowledge of the detail of the science, One great advantage of the mode of treatment is that difficulties of nomenclature, notation, chemical constitution, and even those arising from conventionality of language, are explained as they arise, instead of being massed under the head of "Introductory Chapters," "Preliminary Considerations," or "General Remarks," which are not unfrequently too difficult to be understood by a beginner, too voluminous to be remembered except by the aid of subsequent lessons, and are consequently the cause of much trouble and confusion. This plan has also admitted of greater prominence being given to "The General Principles of Chemical Philosophy," the only section to which the student is asked frequently to return until he finds himself naturally employing those principles in the interpretation of the phenomena obtained by experiment.

An elementary knowledge of the subjects of Gravitation, Heat, Light, Sound, Electricity, and Magnetism cannot be too strongly recommended to the student of Chemistry. The first portion of this manual would have been devoted to an exposition of these branches of physics, so far as they bear on Chemistry, did not the many special books on physics render such a course unnecessary. Quantitative chemical analysis frequently involving determinations of temperature, specific gravity, and atmospheric pressure, a few paragraphs on these subjects are made introductory to the sections on quantitative operations.

The theories that matter consists of molecules and that molecules consist of atoms are freely adopted in this book, the author believing that in the present state of knowledge and education philosophic conceptions regarding Chemistry can only be taught to medical, pharmaceutical, and the great majority of general students by some objective aid.

The chemical notation of the work is in accordance with modern theories. Equations illustrative of pharmacopœial processes have a name attached to each formula.

Chemical nomenclature has been modernized to the extent of defining the alkali-metal salts and the earthy compounds as those of potassium, sodium, ammonium, barium, calcium, magnesium, and aluminium, instead of potash, soda, ammonia, baryta, lime, magnesia, and alumina. The author confidently believes that this change, founded on views now adopted by all prominent writers on Chemistry, and used in the Pharmacopœia of the United States, will be accepted and become popular in medicine and pharmacy. It is a step in the direction of simplicity and consistency, and involves far less hypothesis than is contained in the old system. The name "nitrate of potash," for example, was based on the pure assumption that nitre contained oxide of potassium or potash and nitric anhydride, then erroneously termed nitric acid. By the modern name, "nitrate of potassium," all that is intended to be conveyed is that nitre contains the element common to all potassium compounds and the group of elements common to all nitrates. Under the old method students always experienced difficulty in distinguishing salts of the metal from salts of its oxide—salts of potassium, for instance, from salts of potash; under the new view no such difficulty arises. Names such as potassium nitrate or potassic nitrate are also consistent with modern views, but for general adoption are too unlike the original. The contractions in Latin for names like "nitrate of potassium" are identical with the contractions for names resembling "nitrate of potash;" an accidental circumstance that will much facilitate the general introduction of the former among medical practitioners and pharmacists, and a practical advantage that must determine the choice over the other chemically equivalent names just mentioned. The author ventures to express some gratification that his use and advocacy of this system since the first edition of this manual was published in 1867 has resulted in its adoption, in 1873, in the "Pharmacopœia of the United States," and in the recommendation, from all medical, chemical, and pharmaceutical authorities in Great Britain, of its adoption in the next "British Pharmacopœia." Pharmacy in these two countries will thus sooner or later, in the important matter of chemical nomenclature, be in accord with the current state of chemical science.

The Metric System of Weights and Measures (that which, doubtless, is destined to supersede all others) is alone used in the sections on Quantitative Analysis. In other parts of the manual avoirdupois weights and imperial measures are employed.

It is hoped that the numerous etymological references scattered throughout the following pages will be found useful. Words in Greek have been rendered in English characters, letter for letter. The word "official" is used throughout for things recognized officially by the compilers of Pharmacopœias; "officinal" in its original application to the officina or shop.

Students are strongly recommended to test their progress by frequent examination. To this end appropriate questions are appended to each subject.

The author's ideal of a manual of Chemistry for medical and pharmaceutical students is one in which not only the *science* of Chemistry is taught, but in which the chemistry of every substance having interest for the followers of medicine and pharmacy is noticed at more or less length in proportion to its importance, and at least its position in relation to the leading principles of Chemistry set forth with all attainable exactness. The extent to which he has realized this ideal he leaves to others to decide. Such a work will doubtless in certain parts partake of the character of a dictionary; but this is by no means a fault, especially if a good index be appended; for the points of contact between pure and applied chemistry are thus multiplied, and abundant outlets supplied by which a lover of the science may pass into other chemical domains by aid of other guides, or even into the regions of original research. Among the rarer alkaloids, bitter bodies, glucosides, salts of organic radicals, solid fats, fixed oils, volatile oils, resins, oleo-resins, gum-resins, balsams, and coloring-matters, mentioned in this volume, will be found many such points whence the ardent student may start for the obscure or untrodden paths of scientific chemistry.

Within sixteen years a demand has arisen for ten large editions of this manual. The First, in 1867, was intended as a handbook of practical chemistry only; but the notes and remarks made respecting most of the experiments were found to be so useful by students that this portion of the volume was in the Second Edition (1869) sufficiently extended to render the book more fairly complete in itself. In response to a call from professional friends in the United States in 1870, the work was revised by the author for the followers of medicine and pharmacy in America, the chemistry of the Preparations and Materia Medica of the United States Pharmacopœia being introduced, and such other adaptations included as to form a Third Edition. A Fourth was presented to English workers in the autumn of 1872, and, founded on the Fourth, a Fifth Edition for American students in 1873. A very large Sixth Edition was published in England in 1875, a Seventh in America in 1876, an Eighth in 1879, and a Ninth in England in 1881.

The present (Tenth) edition contains such alterations and additions as seemed necessary for the demonstration of the latest developments of chemical principles and the latest applications of Chemistry in pharmacy. The work now includes the whole of the chemistry of the recently published United States Pharmacopœia, and nearly all the chemistry of the British and Indian Pharmacopœias.

The Index contains eight thousand references.

17 Bloomsbury Square, London,
May 1, 1883.

ADVICE TO STUDENTS.

It is unnecessary to advise you to avoid studying *merely* by way of "preparation for examination." You will not so mistake the means for the end. You are studying to fit yourself for your position in the world. Work diligently, study thoughtfully and deliberately—above all, be thorough; otherwise your knowledge will be transient, and will be unaccompanied by that enlightenment of the understanding, that mental training, mental discipline, and general elevation of the intellect, which constitute, in a word, education. When you are thus educated, you will with ease and pleasure pass any examination in the knowledge you have thus acquired.

All authorities on education, whether statesmen, teachers, or examiners, regard "Examination," even by the most highly skilled "Board," with ample time at its disposal and a wide area from which to select questions, as but a partial test of knowledge and an extremely imperfect test of education. It is the best, however, that has been devised, and is especially useful when, following instead of leading education, it is restricted to the subjects of a well-defined, earnestly-followed, compulsory curriculum of study—a curriculum defined and directed by a competent representative body, wisely administered by properly qualified teachers, and earnestly followed by pupils possessing sound preliminary training.

Students! in all honor and in the highest self-interest take care that any inefficiencies inseparable from "examination" are abundantly compensated by the extent and precision of your knowledge and by the soundness and thoroughness of your whole education.

Apparatus for Experiments in Analysis.

List of Apparatus suitable for a three months' course of practical chemistry in the summer session of medical schools or for any similar series of lessons—including the preparation of elementary gases, analytical reactions of common metals and acidulous radicals, analysis of single salts, chemical toxicology, and the examination of urine, urinary sediments, and calculi:—

One dozen test-tubes.
Test-tube stand.
Test-tube cleaning-brush.
A few pieces of glass tubing, 8 to 16 in. long, with a few inches of India-rubber tubing to fit.
Small flask.
Two small beakers.
Two small funnels.
Two watch-glasses.
Two or three glass rods.
Wash-bottle.
Small pestle and mortar.
A 2-pint earthenware basin.
A 2-inch and a 3-inch evap. basin.
Two porcelain crucibles.
Blowpipe.
Crucible tongs.
Round file.
Triangular file.
Small retort-stand.
Sand-tray.
Wire triangles.
Platinum wire and foil.

Test-paper.
Filter-paper.
Towel.
Two dozen corks.

(*This set, packed in a deal box, can be obtained of any chemical-apparatus maker for about seven dollars.*)

APPARATUS FOR EXPERIMENTS IN SYNTHESIS AND ANALYSIS.

A larger set, suitable for the performance of most of the synthetical as well as analytical experiments described in this manual:—

A set of evaporating-basins, of the following sizes:—
  One 8½-inch.
  One 7¼-inch.
  One 6½-inch.
  One 4-inch.
  Two 3-inch.
One retort-stand and three rings.
Two test-glasses.
One half-pint flask.
One half quire of filter-paper.
Two porcelain crucibles.
One measure-glass, 5 oz.
Blowpipe, 8-inch, Black's.
Two glass funnels.
One doz. test-tubes (German glass).
One test-tube brush.
One pair of 8-inch brass crucible-tongs.
Two soup-plates.
One flat plate.
Two spatula-knives.
One pair of scissors.
One round file.
One triangular file.
One half pound of glass rod.
One half pound of glass tubing.
One ft. small India-rubber tubing.
Three dozen corks of various sizes.
Platinum wire and foil.
Test-papers.
A nest of three beakers.

(*This set, packed in a case, can be obtained of any chemical-apparatus maker for about twelve dollars.*)

A sponge, towels, and note-book may be included.

FURNITURE OF A LABORATORY.

The following apparatus should be ready to the hands of students following an extended course of practical chemistry in a room set apart for the purpose:—

A bench or table and stool.
Water-supply and waste-pipe.
A cupboard attached to a chimney with an outward draught.
A furnace fed with coke; tongs, hot-plate, or sand-bath, etc.
A waste-box.
Shelves for chemicals and other materials in jars or bottles.
Gas-supply and lamp with flexible tube (or a spirit-lamp and spirit).
Test-tube rack, two dozen holes.
Iron stand or cylinder for supporting large dishes.
Iron adapters for fitting dishes to cylinder.
Pestle and mortar, 5 or 6 inches.
One 6-inch funnel.
Brown pan, 1- or 2-gallon.
White jug, 1-gallon.
Water-bottle, quart.
Twenty-eight test-bottles, 6-oz.

Other articles, such as flasks, retorts, receivers, condensers, large evaporating-dishes, may be obtained as wanted. In Quantitative Analysis the apparatus described in the sections on that subject will be required.

REAGENTS.

Certain chemicals are used so frequently in analytical processes that it is desirable to have small quantities placed in bottles in front of the operator. As these "reagents" or "test-solutions" are generally employed in a state of solution, nearly all the solid salts may at once be dissolved (in distilled water). The bottles employed should be well stoppered, and of five or six ounces capacity. The bottles should not be more than three-quarters full; single drops, if required, can then be poured out with ease and precision. The following list of test-solutions is recommended; directions for methods of preparing those not readily purchasable will be found by referring to the Index:—

Sulphuric Acid, strong.
Nitric Acid, strong.
Hydrochloric Acid, strong.
Acetic Acid, strong.
Sol. of Potash, 5 per cent. or B. P.
" Soda, 5 to 15 per cent.
" Ammon., 10 per ct. or B. P.
Lime-water, saturated.

The next nine may contain about 10 per cent. of solid salt:—

Carbonate of Ammonium, with a little solution of Ammonia added.
Chloride of Ammonium.
Phosphate or Arseniate of Ammonium.
Sulphydrate of Ammonium.
Chloride of Barium.
Chloride of Calcium.
Phosphate of Sodium.
Neutral Chromate.

The succeeding seven may have a strength of about 5 per cent.:—

Ferrocyanide of Potassium.
Ferridcyanide of Potassium.
Iodide of Potassium.
Oxalate of Ammonium.
Perchloride of Iron.
Nitrate of Silver.
Perchloride of Platinum.

LIST OF CHEMICALS.

List of chemicals necessary for the practical study of the non-metallic elements mentioned on pp. 13 to 31. The quantities are sufficient for several experiments.

Chlorate of Potassium . .	1 oz.	Phosphorus	½ oz.
Black Oxide of Manganese	1 oz.	Hydrochloric Acid . . .	1 oz.
Zinc	1 oz.	Sulphur	½ oz.
Oil of Vitriol	2 oz.	Iodine	¼ oz.

List of chemicals necessary for the *analytical* study of the metallic and acidulous radicals (pp. 60 to 376). The quantities will depend on the frequency with which experiments are repeated or analyses performed: those mentioned are sufficient for one or two students. The articles are given in the order in which they will be required. The eight substances mentioned in the above list are included:—

The set of test-solutions described on the previous page.	
Carbonate of Potassium	1 oz.
Tartaric Acid	1 oz.
Litmus	¼ oz.
Sulphate of Magnesium	1 oz.
Sulphate of Zinc	1 oz.
Alum	1 oz.
Sulphide of Iron	1 lb.
Oak-galls	1 oz.
Sulphocyanate of Potassium	¼ oz.
White Arsenic	½ oz.
Zinc	½ lb.
Charcoal	½ lb.
Sulphate of Iron	1 oz.
Copper foil	1 oz.
Sulphate of Copper	1 oz.
Tartar Emetic	½ oz.
Mercury	1 oz.
Corrosive Sublimate	½ oz.
Calomel	½ oz.
Tin	1 oz.
Bicarbonate of Sodium	1 oz.
Acetate of Lead	1 oz.
Cyanide of Potassium	½ oz.
Hyposulphite of Sodium	1 oz.
A Lithium Salt	10 grs.
Nitrate of Strontium	¼ oz.
Black Oxide of Manganese	½ lb.
Chloride of Manganese	¼ oz.
Chloride of Cobalt	50 grs.
Nitrate of Nickel	¼ oz.
Chloride of Chromium	¼ oz.
Gold leaves	2 or 3
Chloride of Cadmium	¼ oz.
Nitrate of Bismuth	¼ oz.
Bromide of Potassium	¼ oz.
Starch	1 oz.
Nitrate of Potassium	1 oz.
Copper borings or turnings	1 oz.
Indigo	¼ oz.
Chlorate of Potassium	1 oz.
Iodine	½ oz.
Spirit of Wine	1 oz.
Sulphur	1 oz.
Acid Oxalate of Potassium	1 oz.
Citric Acid	1 oz.
Phosphorus	1 oz.
Borax	1 oz.
Turmeric	1 oz.
Benzoic Acid	50 grs.
Fluor Spar	1 oz.
Tannic Acid	50 grs.
Gallic Acid	50 grs.
Pyrogallic Acid	50 grs.

The quantities of materials required for the study of Chemistry *synthetically* will necessarily vary with the desires and tastes of the operator, or according to the number and requirements of students working together.

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CHEMISTRY:

GENERAL, MEDICAL, AND PHARMACEUTICAL.

INTRODUCTION.[*]

THE infinite variety of solid, liquid, and gaseous substances of which our earth and atmosphere are composed, may be resolved with more or less difficulty into distinct forms of matter appropriately termed Elements, for by no known means can they be further decomposed. Sixty-seven elements have been proved to exist. A few (such as gold) occur naturally in the uncombined state, but the greater number are combined in so subtle a manner as to conceal them from ordinary methods of observation. Thus none of the common properties of water indicate that it is composed of two elements, both gases, but differing much from each other: nor can the senses of sight, touch, and taste, or other common means of examination, detect in their concealment the three elements of which sugar is composed. The art by which these and all other compound substances are resolved into their elements is termed Chemistry, a name derived possibly from the Arabic word *kamai*, to conceal.[†] The *art* of chemistry also includes the construction of compounds from elements, and the conversion of substances of one character into those of another. The general principles or leading truths relating to the elements, to the manner in which they severally combine, and to the properties of the compound substances formed by their union, constitute the *science* of chemistry.*

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[*] Students using this book as a guide in following chemistry practically should read the first three pages, and then commence work by preparing oxygen. All students should read the prefatory pages.

[†] The idea that common metals contained valuable metals concealed within them was the one seed from which mainly sprung chemical knowledge. The men who endeavored to find the secret of such concealment were appropriately termed *alchemists*, and their efforts spoken of as *alchemy* (*al kimia*, from *kamai*, to conceal). Their persistent labors, generation after generation, were unsuccessful so far as the transmutation of baser metals into gold was concerned, yet were invaluable to posterity. For new substances were discovered and truths of nature unveiled; from these discoveries multiplication of discoveries resulted, and thus grew the still-growing branch of knowledge called Chemistry.

From these few words concerning the nature of the art and science of chemistry, it will be seen that in most of the occupations that engage the attention of man chemistry plays an important part—in few more so than in the practice of Therapeutics† and Pharmacy.‡

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* Persons who practise the art and science of Chemistry are known as Chemists. Some two hundred or more years ago, and before chemistry was a science, the "chemists" were the makers or vendors of chemicals, then only used as medicines. They were the successors of the Alchemists. In Great Britain these chemists and the herbalists, otherwise drug-grocers, otherwise druggists, gradually associated to form the "Chemists and Druggists." Between the "Chemist and Druggist" and the Physician there existed the Apothecary—the putter together of medicines or compounder of physicians' prescriptions. The Apothecary has since become a medical practitioner, prescriptions now being "made up" by the Chemist and Druggist. The latter in Great Britain, since the year 1868, has the *title* of *Chemist and Druggist*, his higher title being *Pharmaceutical Chemist;* these respective designations he legally assumes on passing the Minor and Major Examinations, conducted by the Pharmaceutical Society of Great Britain in accordance with the provisions of the Pharmacy Acts of 1852 and 1868. The whole class is often spoken of as that of *Pharmacists* or *Pharmaceutists*, terms also used in the United States. Other classes of chemists are the Analytical Chemists, who give special attention to Analysis: Manufacturing Chemists, who restrict their labors to the preparation of chemicals; while others devote a portion of their knowledge and energies to Chemical Education or to Chemical Research, or are appealed to as Consulting Chemists by the persons, firms, corporations, or governments needing chemical advice respecting industrial processes, hygienic matters, etc. The callings of the Consulting and Analytical Chemist are generally united, and the professional gentlemen who follow these conjoint avocations also not unfrequently occupy professorial or other tutorial positions, sometimes adding to these labors more or less work at original chemical research. In England, Scotland, and Ireland, nearly all the leading professional chemists are *Fellows of the Institute of Chemistry of Great Britain and Ireland.*

† Therapeutics (*θεραπευτικος*, *therapeutikos*, from *θέραπευω*, *therapeuo*, to nurse, serve, or cure) is that branch of medicine which treats of the application of remedies for diseases; it includes dietetics. The therapeutist also takes cognizance of hygiene, that department of medicine which respects the preservation of health.

‡ Pharmacy (from *φάρμακον*, *pharmakon*, a drug) is the generic name for the operations of preparing or compounding medicines, whether performed by the Medical Practitioner or by the Chemist and Druggist. It is also sometimes applied, like the corresponding term "Surgery," to the apartment in which the operations are conducted.

Air, water, food, drugs, and chemicals, in short all material substances, are composed of a few elements. An intimate knowledge of the properties of these, and of the various substances they form by combining with each other, a knowledge of the power or force (the chemical force, or chemical affinity) by which the elements contained in those compounds are held together, and an application of such knowledge to Pharmacy and Medicine, must be the objects sought to be attained by the learner, for whom this work has been especially written.

The Elements.—Of the sixty-seven known elements thirty-nine are of medical or pharmaceutical interest; of these, about two-thirds are metals, and one-third non-metals; the remainder* are so seldom met with in nature as to have received no practical application either in medicine, art, or manufacture. Before intimately studying the elements, it is desirable to acquire some general notions concerning them: such a procedure will also serve to introduce the practical student to his apparatus, and make him better acquainted with the various methods of manipulation.†

Metallic Elements.—With regard to the metallic elements, it may be safely assumed that the reader has sufficient knowledge for present purposes; but little, therefore, need now be said respecting them. He has an idea of the appearance, relative weight, hardness, etc., of such metals as gold, silver, copper, lead, tin, zinc and iron. If he has not a similar knowledge of mercury, antimony, arsenicum, platinum, nickel, aluminium, magnesium, potassium, and sodium, he should commence his studies by seeing and handling specimens of each of these metals.

Non-Metallic Elements.‡—With regard to the non-metallic elements, it is here supposed that the student has no general knowledge. He should commence his studies therefore by a series of operations as follows, on eight out of their number.

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* A complete list of the elements will be found at the end of the volume.

† This allusion to apparatus need not discourage the youngest pupil. With the aid of a few phials, wine-glasses, or other similar vessels always at hand, he may, by studying the following pages, learn the chemical reactions which are constantly occurring in the course of making up medicines, understand the process by which medicinal preparations are manufactured, and detect adulterations, impurities, or faults of manufacture. Among the substances used in medicine, will be found nearly all the chemicals required. If, in addition, a dozen test-tubes and a few feet of glass tubing be procured, many of the experiments described may be performed. For full lists of apparatus and chemicals see introductory pages.

‡ These bodies are sometimes termed *metalloids* (from *μέταλλον*, *metallon*, a metal, and *εἰδος*, *eidos*, likeness); but the name is not appropriate, for the non-metallic elements have no likeness to metals.

OXYGEN.

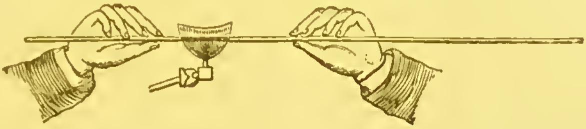
Preparation.—As oxygen is the most abundant element in nature, forming, though in a combined state, about one-half of the whole weight of our globe, it may safely be assumed that this element can readily be obtained in the free condition in a state of purity. In fact, the air itself contains about one-fifth of its bulk of oxygen, though from the air it cannot be separated, at least not easily and readily, for experimental purposes. It is preferable to apply heat—that force which will often be noticed as antagonistic, so to speak, to chemical union; heat generally separating particles of matter further from each other, while chemical attraction tends to bind them closer together—it is better to heat certain compounds containing oxygen; the latter is then evolved in its normal, natural condition of gas. Several substances, when heated, yield oxygen; but for convenience and economy, the crystalline body known as chlorate of potassium is best fitted for the experiment. The size and form of the vessel in which to heat it will mainly depend on the quantity required; but for the purposes of the student the best is a *test-tube*, an instrument in constant requisition in studying practical chemistry. It is simply a thin tube of glass, a few inches in length, and half or three-quarters of an inch in diameter, closed by fusion at one end. It is made of thin glass, in order that it may be rapidly heated or cooled without risk of fracture. (See Fig. 1.)

Outline of the Process.—Heat chlorate of potassium (say, as much as will lie on a shilling) in a test-tube, by means of a spirit- or gas-flame; gaseous oxygen is quickly envolved. Before applying heat, however, provision should be made for collecting the gas. (See Fig. 3.)

Collection of Gases.—Procure a piece of glass tubing about the thickness of a quill pen, and a foot or eighteen inches long, and fit it accurately to the test-tube by means of a cork. (Longer tubes may be neatly cut to any size by smartly drawing the edge of a triangular file across the glass at the required point, then clasping the tube, the scratch being between the hands, and pulling the portions asunder, force being exerted in a *slightly* curved direction so as to open out the crack which the file has commenced.) The tube is fixed in the cork through a round hole made by the aid of a red-hot wire, or, better, a rat-tail file, or, best of all, by one of a set of cork-borers—pieces of brass tubing sharpened at one end and having a flat head at the other. Setting aside the test-tube for a few minutes, proceed to bend the long piece of tubing to the most convenient shape for collecting the gas.

To Bend Glass Tubes.—Hold the part of the tube required to be bent in any gas- or spirit-flame (a fish-tail gas-jet answers very well), constantly rotating it, so that about an inch of the glass becomes heated. It will soon be felt to soften, and will then, yielding to the *gentle* pressure of the fingers, assume any required angle. In the present case, the tube should be heated at about four inches from the extremity to which the cork is attached, and bent to an angle of about 90 degrees.

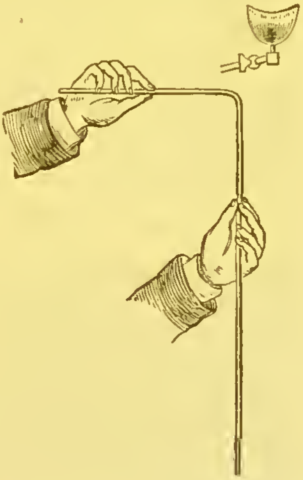
Fig. 1.



Softening and bending Glass Tubes.

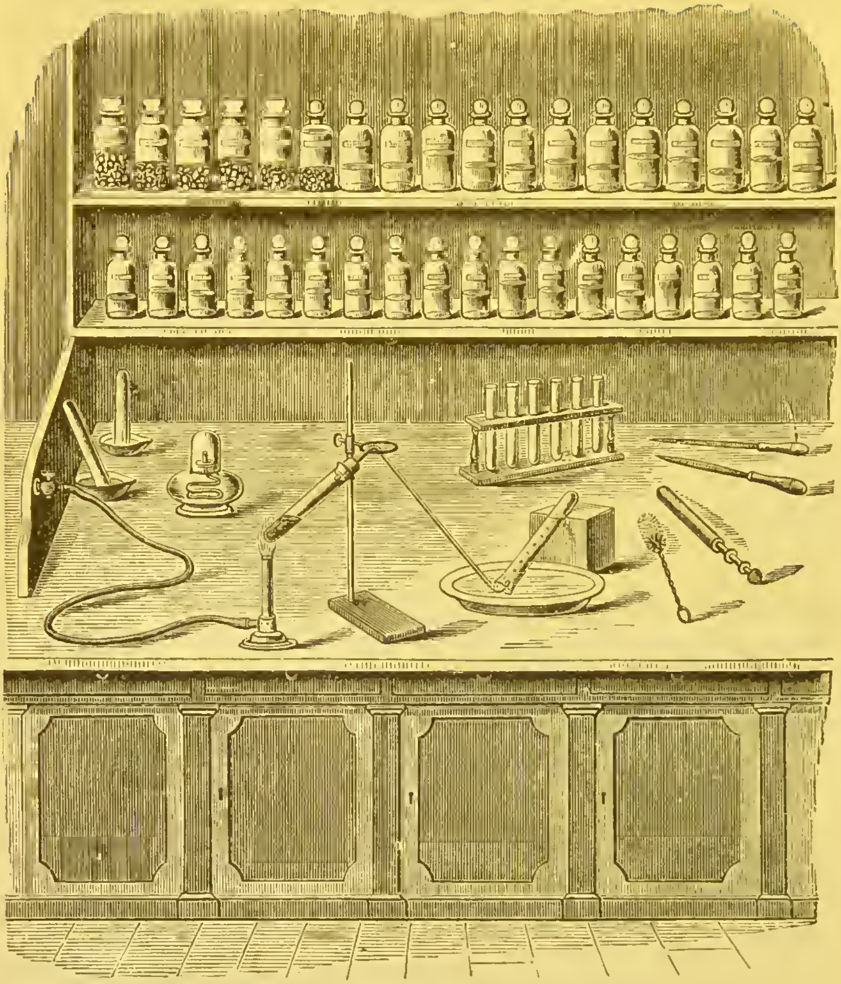
Source of Heat.—The source of heat for the test-tube may be the flame of an ordinary spirit-lamp, or, still better where coal-gas is procurable, a mixture of the latter with air. Gas-lamps especially constructed to burn a mixture of coal-gas and air are sold by chemical-apparatus manufacturers. (See Figs. 3 and 7).

Fig. 2.



Collection, etc. (continued).—Fit the cork and bent tube into the test-tube; the apparatus will then be ready for delivering gas at a convenient distance from the heated portion of the arrangement. To collect it, have ready three or four test-tubes (or small wide-mouthed bottles) filled with water, and inverted in a basin, or other similar vessel, also containing water, taking care to keep the mouths of the tubes a little below the surface. Now apply heat to the chlorate contained in the test-tube, and so arrange the open end of the bent tube under the water that the gas which presently issues may bubble into and gradually fill the inverted test-tubes. The first tubeful may be rejected, as it probably consists of little more than the air originally in the apparatus, and which has been displaced by the oxygen. That which comes afterwards will be pure oxygen.

Fig. 3.



This engraving represents the preparation, collection, and storage of small quantities of oxygen gas. A test-tube and bent glass tube, joined together by a perforated cork, are supported by the arm of an iron stand. (The apparatus might be held by the fingers.) The tube is heated by a gas-lamp. (The spirit-lamp shown at the back might be used instead.) Gas evolved from the heated substance in the test-tube is displacing water from an inverted test-tube. Spare tubes in a test-tube rack are at hand, and tubes already filled are set aside till wanted. A nest of cork-borers, a round file, a triangular file, and a test-tube cleaning brush are lying on the table or student's bench. Below are cupboards for apparatus, above are bottles containing testing liquids, etc.

As each tube or bottle becomes full, its mouth (still under the surface of the water) may be closed by a cork and set aside; or a little cup (such as a porcelain crucible or small gallipot) may be brought under the mouth, and the cup, with the mouth of the tube in it, be lifted out of the water and placed close by till wanted, the water remaining in the cup effectually preventing the gas from escaping.

On the large scale, oxygen may be made in the same way, larger vessels (glass flasks or iron bottles) being employed. Less heat also will be necessary if the chlorate of potassium be previously mixed with very fine sand, or, still better, with about an equal weight of common black oxide of manganese.

Note on the Collection and Storage of Gases.—It may be as well to state that nearly all gases, whether for experimental or practical purposes, are collected and stored in a similar manner. Even coal-gas is generated at gas-works in iron retorts very much the shape of test-tubes, only they are as many feet long as a test-tube is inches: and the well-known gigantic gas-holders may be viewed as inverted iron test-tubes of great diameter.

Properties.—Oxygen is a colorless gas. Cailletet and Pictet succeeded in liquefying it. Wroblewski and Olszewski have obtained it in some amount as a definite, colorless, transparent fluid. Obviously it is not very soluble in water, or it could not be collected by the aid of that liquid.

Oxygen is soluble to a certain extent, however (about 3 volumes in 100 at common temperatures), or fishes could not breathe.

Other noticeable features are its want of taste and smell. Next, to show the relation of oxygen to combustion, remove one of the tubes from the water by placing the thumb over its mouth, apply for a second a lighted wood match to the orifice; the gas will be found to be incombustible. Extinguish the flame of the match, and then quickly introduce the still incandescent carbonaceous extremity of the wood half-way down the test-tube; the wood will at once burst into flame owing to the extreme violence with which oxygen supports combustion. These tests of the presence of oxygen may also be applied at the extremity of the delivery-tube whilst the gas is being evolved. (It is desirable to retain two tubes of the gas for use in subsequent experiments; also one tube in which only one-third of the water has been displaced by oxygen.)

Relation of Oxygen to Animal and Vegetable Life.—Not only the carbon at the end of a piece of charred wood, but any other substance that will burn in air (which, as will be seen presently, is diluted oxygen) will burn more brilliantly in pure oxygen. The warmth of the body of animals is kept up by the continuous burning of the tissues in the oxygen (of the air) drawn into the system through the lungs. The product of this combustion is a gaseous compound of carbon and oxygen termed carbonic acid gas, a gas which, in sunlight, is decomposed in the cells of plants, with fixation of the carbon and liberation of the oxygen; hence the atmosphere is kept constant in composition.

Memorandum.—At present it is not advisable that the reader should trouble himself with the consideration of the chemical action which occurs either in the elimination of oxygen from its compounds, or in the separation of any of the following non-metallic elements from their combinations. It is to the properties of the elements themselves that he should restrict his attention. Working thus from simple to more complex facts, he will in due time find that the comprehension of such actions as occur in the preparation of these few elements will be easier than if he attempted their full study now.

HYDROGEN.

Preparation and Collection.—The element hydrogen is also a gas,* and is obtainable from its commonest compound, water (of which one-ninth by weight is hydrogen), by the agency of hot zinc or iron, but more conveniently by the action of either of these metals on cold diluted sulphuric acid. The apparatus used for making oxygen may be employed for this experiment; but no lamp is required. Place several pieces of thin zinc † in the generating-tube (Fig. 4), or in any common glass bottle (Fig. 5) or flask, and cover them with water. The collecting-tubes (these may be wide-mouthed bottles) being ready, add strong sulphuric acid (oil of vitriol) to the zinc and water, in the proportion of about one volume of acid to five of water, and fit on the delivery-tube, or pour the acid down such a funnel-tube ‡ as is shown in Fig. 5; the hydrogen is at once evolved. Having rejected the first portions (or having waited until the air originally in the bottle may be considered to be all expelled), collect four or five tubes of the gas in the manner described under Oxygen.

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* Graham obtained alloys of hydrogen with palladium and other metals, compounds in which several hundred times its bulk of gas is retained by the metal in vacuo or even at a red heat. This was physical confirmation of the opinion long held by chemists, that hydrogen is a gaseous metal. Graham termed it hydrogenium (other chemists *hydrium*), and considered its relative weight in the solid state to be nearly three-fourths that of water. Cailletet and Pictet have since actually liquefied and solidified this element.

† The best form is *granulated zinc* (*Zincum*, U. S. P.), made by heating scraps of common sheet zinc in a ladle over a fire, and as soon as melted pouring, in a slow stream, into a pail of water from a height of 8 or 10 feet. Each drop of zinc thus yields a thin little bell, which, for its weight, presents a large surface to the action of the acid water. If the zinc is allowed to become hotter than necessary, the little bells will not be formed.

‡ Funnel-tubes may be purchased of the apparatus-maker, or, if the pupil has access to a table blowpipe and the advantage of a tutor to direct his operations, they may be made by himself.

Fig. 4.

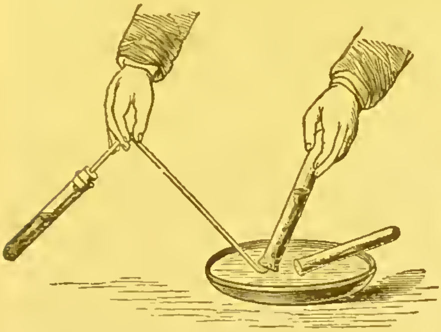
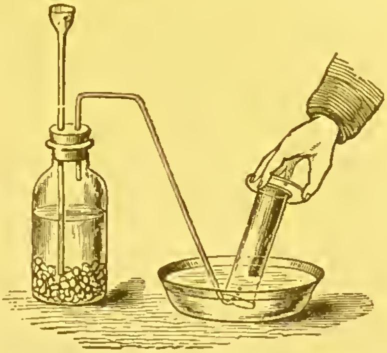


Fig. 5.



Preparation of Hydrogen.

In making larger quantities bottles of appropriate size may be employed.

Other metals, notably potassium and sodium, liberate hydrogen the moment they come into contact with water; but the processes are not economical.

Properties.—Like oxygen, hydrogen gas is invisible, inodorous, and tasteless. If made with iron it has a strong smell, but this is due to impurities derived from the iron.

Apply a flame to the mouth of the delivery-tube (care being taken that the gas is coming off briskly—a guarantee that no air remains in the generating vessel); ignition of the hydrogen ensues, showing that, unlike oxygen, it is combustible.

Plunge a lighted match well into a tube (or wide-mouthed bottle) containing hydrogen; the gas is ignited, but the match becomes extinguished. This shows that hydrogen is not a supporter of combustion.

Hydrogen in burning unites with the oxygen of the air and forms water, which may be condensed on a cool glass or other surface. Prove this by holding a glass vessel a few inches above a hydrogen flame. In burning the hydrogen contained in one of the tubes or bottles, the flame is best seen when the tube is held mouth upwards, and water poured in so as to force out the gas gradually.

If, instead of this gradual combination of the two elements oxygen and hydrogen, they be mixed together in bulk in the right proportions and then ignited, they will rapidly combine, and explosion will result. Prepare a mixture of this kind by filling up with hydrogen a test-tube from which one-third of the water has been expelled by oxygen. Remove the tube from the water, placing a finger over the mouth, and, having a lighted match ready, apply the flame ; a slight explosion ensues, owing to the instantaneous combination of the two elements, and the expansive force of the highly heated steam produced. If anything larger than a test-tube is employed in this experiment, it should be a soda-water bottle, or some such vessel equally strong.

These two gases thus unite at a temperature far higher than that of boiling water, two volumes of hydrogen and one of oxygen yielding two volumes of gaseous water (true steam).

The noise of such explosions is caused by concussion between the suddenly expanded gaseous body and the air.

The force of the explosion, or, in other words, the force of the suddenly heated, and therefore suddenly expanded, steam, is below that necessary to break the test-tube. Some force, however, is exerted, and hence the necessity of the precaution previously suggested of allowing all the air which may be in a hydrogen-apparatus to escape before proceeding with the experiments. If a flame be applied to the delivery-tube before all the air is expelled, the probable result will be ignition of the mixture of hydrogen and oxygen (of the air) and consequent explosion. But even in this case the generating-vessel is not often fractured unless it be large and of thin glass, the ordinary effect being that the cork is blown out, and the delivery-tube broken on falling to the ground.

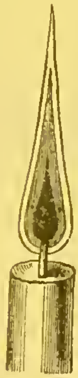
Hydrogen is a prominent constituent of all the substances used for producing artificial light, such as tallow, oil, and coal-gas. The explosive force of large quantities, such as a roomful of coal-gas and air, though vastly below that of an equal weight of gunpowder, is well known to be sufficient at least to blow out that side of the room which offers least resistance.

The composition of water can be proved analytically as well as synthetically, a current of electricity decomposing it into its constituent gases, twice as much hydrogen as oxygen, by volume, being produced.

Combustion (from *comburo*, to burn).—The experiments with hydrogen and oxygen illustrate the true character of combustion. Whenever chemical combination is sufficiently intense to be accompanied by heat and light, the materials are said to undergo combustion. Combustion only occurs at the line of contact of the combining bodies ; a jet of oxygen will burn in an atmosphere of hydrogen quite as easily as a jet of hydrogen in oxygen. A jet of air (diluted oxygen) will burn as readily in a jar of coal-gas as a jet of coal-gas burns in air ; each is combustible, each supports the combustion of the other. Hence the terms *combustible* and *supporter of combustion* are purely conventional, and only applicable so long as the circumstances under which they are applied remain the same. In the case of substances burning in air, the conditions are, practically, always the same: hence no confusion arises from regarding air as the great supporter of combustion, and bodies which burn in it as being combustible.

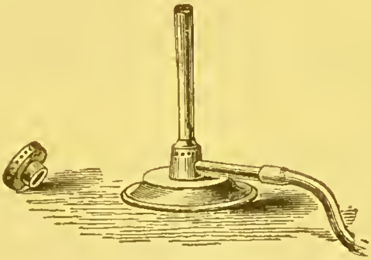
Structure of Flame.—A candle-flame or oil-flame is a jet of gas intensely heated; the central portion is unburnt gas; the next envelope is formed of partially burnt and very dense, gaseous, and solid particles sufficiently highly heated to give light, and the outer cone of completely burnt gases. In the figure the sharpness of limit of these cones is purposely somewhat exaggerated. Air made, by any mechanical contrivance of burner, to mix with the interior of a flame at once burns up, or perhaps prevents the formation of dense gases giving a hotter, but non-luminous, jet. The air-gas lamps (Fig. 7), or "Bunsen" gas-burners commonly used in chemical laboratories are constructed on this principle; their flame has the additional advantage of not yielding a deposition of soot.

Fig. 6.



Structure of Flame.

Fig. 7.



"Bunsen" or Air-gas Burner.

In the air-gas lamp, coal-gas escaping from a small orifice draws rather more than twice its volume of air (supplied through adjacent holes) into its column, and the mixture of gas and air passes upwards along a pipe. It only burns at the end, and not within the pipe, partly because the metal of the burner, by conducting heat away, cools the mixture below the temperature at which it can ignite; partly because the velocity with which the mixture flows out is greater than the rate at which such a mixture ignites; and partly because the proportion of air to gas in this mixture is insufficient for thorough and perfect combustion, the external air contributing materially to the complete combustion of the jet of air-gas. The *Davy safety-lamp* acts on the first-named principle; a wire-gauze cage surrounds an oil-flame; an inflammable mixture of gas and air (fire-damp) can pass through the gauze and catch fire and burn inside; but the flame cannot be communicated to the mixture outside, because the metal of the gauze and of the other parts cools down the gas below the temperature at which combustion can continue.

Properties (continued).—Gaseous hydrogen is the lightest substance known. It was formerly used for filling balloons, but was superseded by coal-gas. Coal-gas is not so light as hydrogen, but is cheaper and more easily obtained. The lightness of hydrogen may be rendered evident by the following experiment: Fill two test-tubes with the gas, and hold one with its mouth downwards and the other with its mouth upwards. The hydrogen will have escaped from the latter in a few seconds, whereas the former will still contain the gas after the lapse of some minutes. This may be proved by applying a lighted match to the mouths of the respective tubes.

The relative weight or specific gravity of oxygen is sixteen times that of hydrogen. A vessel holding one grain of hydrogen will hold sixteen grains of oxygen. The relation of the weight of hydrogen to air is as 1 to 14.44 or as 0.0693 to 1.0. One grain of hydrogen by weight would measure about 27 fluidounces. One grain of hydrogen would, therefore, about fill a common wine bottle. Such a bottle would hold about 14½ grains of air, or 16 grains of oxygen.

Mem.—It is desirable to retain two tubes of hydrogen for use in subsequent experiments.

Diffusion of Gases.—Hydrogen cannot be kept in such vessels as the inverted test-tubes; for, though much lighter than air, it *diffuses* downwards into the air, while the air, though much heavier, diffuses upwards into the hydrogen. This power of *diffusion* is characteristic of all gases, and proceeds according to a fixed law, namely, "in inverse proportion to the square root of the specific gravity of the gas" (Graham). Thus hydrogen diffuses four times faster than oxygen. This great and important property of diffusion strongly suggests that the particles of gases, at least, are always moving, never at rest; how otherwise *could* gases diffuse into each other, as they do, notwithstanding the opposing influence of gravitation? Diffusion strongly supports this (Clausius's) Kinetic (*κινέω*, *kineō*, I move or put in motion) theory of the physical condition of gases.

PHOSPHORUS.

Appearance and Source.—Phosphorus (*Phosphorus*, U. S. P.) is a solid element, in appearance and consistence resembling white wax; but it gradually becomes yellow by exposure to light. It is a characteristic constituent of bones, and is always prepared from that source by a process which will be subsequently described.

Caution.—Phosphorus, on account of its great affinity for oxygen, takes fire very readily in the air, and should therefore be kept under water. When wanted for use it must be cut under water. It is employed in tipping lucifers, though *red* or *amorphous phosphorus* (*vide* Index) is least objectionable for this purpose.

Experiment.—Dry a piece about one-fourth the size of a pea by quickly and carefully pressing it between the folds of porous (filter or blotting) paper; place it on a plate, and ignite by touching it with a piece of warm wire or wood. The product of combustion is a dense white suffocating smoke, which must be confined at once by placing an inverted tumbler, test-glass, or other similar vessel over the phosphorus. The fumes rapidly aggregate, and fall in white flakes on the plate. When this has taken place, and the phosphorus is no longer burning, moisten the powder with a drop or two of water, and observe that some of the water is converted into steam, an effect due to the intense affinity with which the two combine.

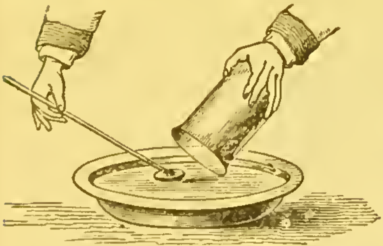
The powder produced by the combustion of phosphorus is phosphoric anhydride; the combination of the latter with the elements of water produces a variety of phosphoric acid which dissolves in the water, forming on standing a dilute solution of ordinary phosphoric acid. The Diluted Phosphoric Acid of the British and United States Pharmacopœias is a somewhat similar solution, made, however, in a different way, and of a definite strength.

NITROGEN.

Source.—The chief source of this gaseous element is the atmosphere, nearly four-fifths of which consists of nitrogen (the remaining fifth being almost entirely oxygen).

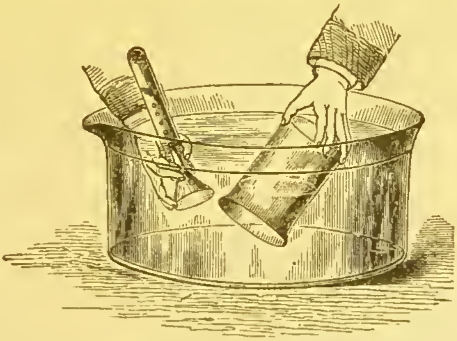
Preparation.—Burn a piece of dried phosphorus, the size of a pea, in a confined portion of air. The oxygen is thus removed, and nitrogen alone remains. The readiest mode of performing this experiment is to fix a piece of earthenware (the lid of a small porcelain crucible answers very well) on a thin piece of cork, so that it may float in a dish of water. Place the phosphorus on the lid, ignite by a warm rod, and then invert a tumbler, or any glass vessel of about a half-pint capacity, over the burning phosphorus, so that the glass may dip into the

Fig. 8.



Preparation of Nitrogen.

Fig. 9.



Decantation of Gases.

water. Let the arrangement rest for a short time for the fumes of phosphoric anhydride to subside and dissolve in the water, and then decant the gas into test-tubes in the manner indicated in Fig. 9, using a tub or other vessel of water of sufficient depth to permit the glass containing the nitrogen to be turned on one side without air gaining access.

Larger quantities of nitrogen are made in the same way. Other combustibles, such as sulphur or a candle, might be used to burn out the oxygen from a given quantity of air, but none answer so quickly and completely as phosphorus; added to which, the product of their combustion would not always be dissolved by water, but would remain with and contaminate the nitrogen.

Mem.—The statement concerning the composition of the air is roughly confirmed in preparing nitrogen, about one-fifth of the volume of the air originally in the glass vessel having disappeared, its place being occupied by water from the dish.

Properties.—Like oxygen and hydrogen, nitrogen gas is invisible, tasteless, and inodorous. By pressure Cailletet and Pictet succeeded in condensing it to a liquid. Wroblewski and Olszewski have obtained it in some amount as a definite, colorless, transparent fluid. It is only slightly soluble in water. Free nitrogen is distinguished from all other gases by the absence of any characteristic or positive properties. Apply a flame to some contained in a tube; it will be found to be incombustible. Immerse a lighted match in the gas; the flame is extinguished, showing that nitrogen is a non-supporter of combustion.

The chief office of nitrogen in the air is to dilute the energetic oxygen, a mere *mechanical* mixture resulting.

Nitrogen is fourteen times as heavy as hydrogen.

The air is nearly fourteen and a half (14.44) times as heavy as hydrogen. Its average composition, including minor constituents, which will be referred to subsequently, is as follows:—

Composition of the Atmosphere.

	In 100 volumes.
Oxygen	20.61
Nitrogen	77.95
Carbonic acid gas	.04
Aqueous vapor	1.40
Nitric acid	traces.
Ammonia	
Carburetted hydrogen	
Sulphuretted hydrogen	traces in towns.
Sulphurous acid	

The above proportions are by volume. By weight there will be nearly 23 parts of oxygen to nearly 77 of nitrogen, oxygen being the heavier in the ratio of 16 to 14. Ozone (*vide* Index) is also said to be a normal constituent of air.

The comparative inactivity or negative character of nitrogen in its free condition, that is, when uncombined with other elements, contrasts strongly with its apparent influence in a state of combination. When its compounds with hydrogen come to be studied, it will be found to be, apparently, the chief, or leading, or, in a sense, the most important element of those compounds—the ammoniacal compounds. United with carbon it gives the poisonous cyanic substances. With oxygen it gives quite a large group of bodies, amongst which are the common and important class of salts termed nitrates. With carbon as well as hydrogen and some oxygen it affords powerful agents termed alkaloids—near relatives of ammonia—while the same elements otherwise grouped, with sometimes a little sulphur or phosphorus, form the various albumenoid and gelatinoid matters characteristic of the tissues of animals and vegetables. In a perfect structure we should perhaps scarcely regard any one element or member as more important than another, still such a conclusion almost forces itself upon us as we become acquainted with the chemical history of combined nitrogen.

CHLORINE.

Source.—This element is a gas. Its chief source is common salt, more than half of which is chlorine.

Preparation.—About a quarter of an ounce of salt and the same amount of black oxide of manganese are mixed, and placed in a test-tube with sufficient water to cover them; on adding a small quantity of sulphuric acid, the evolution of chlorine commences. For mode of collection see following paragraphs.

Fig. 10.

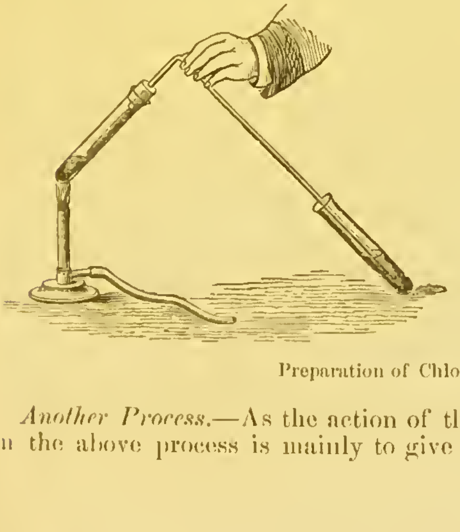
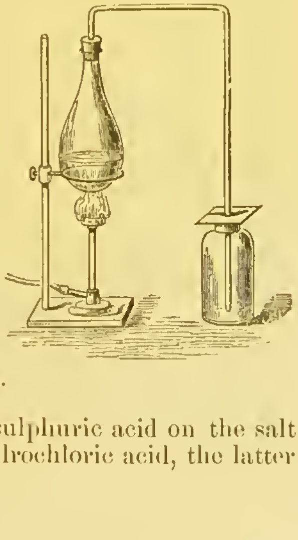


Fig. 11.



Preparation of Chlorine.

Another Process.—As the action of the sulphuric acid on the salt in the above process is mainly to give hydrochloric acid, the latter acid (about 4 parts) and the black oxide of manganese (about 1 part) may be used in making the gas, instead of salt, sulphuric acid, and black oxide of manganese. This, the usual process, is that adopted in the British and United States Pharmacopœias.

Collection and Properties.—Chlorine is a most suffocating gas. Great care must consequently be observed in experimenting with this element. As soon as its penetrating odor indicates that it is escaping from the test-tube, the cork and delivery-tube (similar to that used in making oxygen) should be fitted on, and the gas allowed to pass to the bottom of another test-tube containing water (Fig 10). When thirty or forty small bubbles have passed, their evolution being assisted by slightly heating the generating-tube, the latter should be removed to the cupboard usually provided in laboratories for performing operations with noxious gases, or dismounted, and the contents washed away. The water in the collecting-tube will now be found to smell of the gas, chlorine being, in fact, soluble in about half its bulk of water. Chlorine-water is official* in the United States Pharmacopœia (*Aqua Chlori*, U. S. P.).

Larger quantities may be made from hydrochloric acid and black oxide of manganese (about 4 parts to 1) in a Florence flask, fitted with a delivery-tube, the flask being supported over a flame by the ring of a retort-stand or any similar mechanical contrivance (Fig. 11). A piece of cardboard on the neck of the collecting-bottle, as indicated in the figure, retards diffusion of the gas from the bottle during collection of the gas.

Mem.—Flasks and similar glass vessels are less liable to fracture if protected from the direct action of the flame by being placed on a piece of wire gauze 3 to 4 inches square, or on a *sand-bath*, that is, a saucer-shaped tray of sheet iron, on which a *thin* layer of sand is placed.

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* The Pharmacopœia and all in it are official (*office*, Fr., from L. *officium*, an office). There are many things which in pharmacy are officinal (Fr., from L. *officina*, a shop) but not official. To restrict the word *officinal* to the contents of a pharmacist's shop and to that portion of the contents which is Pharmacopœial, is radically wrong, and should be avoided. "An *official* formula is one given under authority. An *officinal* formula is one made in obedience to the customary usage of the shop (*officina*). To state that any preparation under the sanction of the Pharmacopœia is officinal, is a misapprehension of the meaning of the word."—*J. Brough.*

That is *official* which emanates from a recognized authority. That is *officinal* which is issued from an *officina* or workshop —*Joseph Ince.*

Official writings and orders are those issued by official persons. *Officinal* articles are such as are found in a shop.—*J. F. Stanford, M.A., F.R.S.*

The *Vapor Chlori*, B. P., or Inhalation of Chlorine, is simply moist chlorinated lime so placed that some of the chlorine given off may be inhaled.

During these manipulations the operator will have noticed that chlorine is of a light-green color. That tint is readily observed when the gas is collected in large vessels. As it is soluble in water (2⅓ vols. in 1 vol. at 60° F.), it cannot be economically stored over that liquid. Being, however, nearly twice and a half as heavy as air, it may be collected by simply allowing the delivery-tube to pass to the bottom of the test-tube or dry bottle (Fig. 11).

The distinctive property of chlorine is its bleaching power. Prepare some colored liquid by placing a few chips of logwood or other dyeing material in a test-tube half full of hot water. Pour off some of this red decoction into another tube and add a few drops of the chlorine-water; the red color is rapidly destroyed.

Chlorine readily decomposes offensive effluvia; it is one of the most powerful of the *deodorizers*. It also decomposes putrid and infectious matter; it is one of the best of *disinfectants*. (*Antiseptics* are substances which *prevent* putrefaction. See Index.)

Combination of Hydrogen with Chlorine, forming Hydrochloric Acid.—If an opportunity occurs of generating the gas in a closed chamber or in the open air, a test-tube, of the same size as one of those in which hydrogen has been retained from a previous operation, is filled with the gas. The hydrogen tube is then inverted over that containing the chlorine, the mouths being kept together by encircling them with a finger. After the gases have mixed, the mouths of the tubes are quickly in succession brought near a flame, when explosion occurs, and fumes of a compound of hydrochloric acid with the moisture of the air are formed. The Hydrochloric Acid of Pharmacy (*Acidum Hydrochloricum*, U. S. P.) is a solution of the gas (made in a more economical way) in water.

The foregoing experiment affords evidence of the powerful affinity of chlorine and hydrogen for each other. Chlorine dissolved in water will, in sunlight, slowly remove hydrogen from some of the water and liberate oxygen. The bleaching power of chlorine is generally referred to this oxidizing effect which it produces in presence of water; for dry chlorine does not bleach.

Density.—Chlorine is thirty-five and a half times as heavy as hydrogen. A wine bottle would hold about 35½ grains.

SULPHUR, CARBON, IODINE.

The physical properties of these elements (color, hardness, weight, etc.) are familiar. Their leading chemical characters will also be understood when a few facts concerning each are made the subject of experiment.

Sulphur.—Burn a small piece of sulphur; a penetrating odor is produced, due to the formation of a colorless gas, the same as that formed on igniting a sulphur-tipped lucifer match.

This product is a perfectly definite chemical compound of the oxygen of the air with the sulphur. It is termed sulphurous anhydride or sulphurous acid gas.

Carbon is familiar in the forms of soot, coke, charcoal, graphite (or plumbago, popularly termed blacklead), and diamond. The presence of carbon in wood, and in other vegetable and animal matter, is at once rendered evident by heat. Place a little tartaric acid on the end of a knife in a flame; the blackening that occurs is due to the separation of carbon. The black matter at the extremity of a piece of half-burned wood is also carbon.

Carbon, like hydrogen, phosphorus, and sulphur, has a great affinity for oxygen at high temperatures. A striking evidence of that affinity is the evolution of sufficient heat to make the materials concerned red or even white hot. When ignited in the dilute oxygen of the air, carbon simply burns with a moderate glow, as seen in an ordinary coke or charcoal fire, but when ignited in pure oxygen, the intensity of its combination is greatly exalted. The product of the combination of the two elements, if the oxygen be in excess, is an invisible gaseous body termed carbonic acid gas: if the carbon be in excess, another invisible gas termed carbonic oxide results.

Iodine.—A prominent chemical characteristic of iodine is its great affinity for metals. Place a piece of iodine, about the size of a pea, in a test-tube with a small quantity of water, and add a few iron-filings or small nails. On gently warming this *mechanical* mixture, or even shaking if longer time be allowed, the color and odor of the iodine disappear: it has *chemically* combined with the iron: a *chemical compound* has been produced. If the solution be filtered, a clear aqueous solution of the compound of the two elements is obtained.

This compound is an iodide of iron. Its solution, made as above, and mixed with sugar, forms, when of a strength of 10 per cent., the ordinary Syrup of Iodide of Iron of pharmacy (*Syrupus Ferri Iodidi*, U. S. P.). A strong solution mixed with sugar, glycyrrhiza, gum, etc., constitutes the corresponding Pill (*Pilulæ Ferri Iodidi*, U. S. P.). The solid iodide (*Ferri Iodidum*, B. P.) is obtained on removing the water of the above solution by evaporation.

Sulphur and *Iron*, also, when very strongly heated, *chemically combine* to form a substance which has none of the properties of a *mixture* of sulphur and iron—that is, has none of the characters of sulphur and none of iron, but new properties altogether. The product is termed Sulphide of Iron. Its manufacture and uses will be alluded to in treating of the compounds of iron; it is mentioned here as a simple but striking illustration of the difference between a *chemical compound* and a *mechanical mixture*.

THE ELEMENTS, THEIR SYMBOLS, Etc.

From the foregoing statements a general idea will have been obtained of the nature of several of the more frequently occurring elements. Some additional facts concerning them may be gathered from the following Table, which gives the name in full, the symbol (or short-hand character)* of the name, and its origin.

For the purposes of study the elements may be divided into three classes—viz., those frequently used in pharmacy, those seldom, and those never used.

Name.	Symbol.	Derivation of Name.
Oxygen	O	From ὀξὺς (oxūs), *acid*, and γένεσις (genesis), *generation*, i. e., generator of acids. It was supposed to enter into the composition of all acids when first discovered.
Hydrogen . . .	H	From ὕδωρ (hudōr), *water*, and γένεσις (genesis), *generation*, in allusion to the product of its combination in air.
Nitrogen	N	From νίτρον (nitron), and γένεσις (genesis), *generator of nitre.*
Carbon	C	From *carbo*, *coal*, which is chiefly carbon.
Chlorine	Cl	From χλωρὸς (chlōros), *green*, the color of this element.
Iodine	I	From ἴον (ion), *a violet*, and εἶδος (eidos), *likeness*, in reference to the color of its vapor.
Sulphur	S	From *sal*, a *salt*, and πῦρ (pūr), *fire*, indicating its combustible qualities. Its common name, *brimstone*, has the same meaning, being the slightly altered Saxon word *brynstone*, i. e., burnstone.
Phosphorus . . .	P	φῶς (phōs), *light*, and φέρειν (pherein), *to bear*. The light it emits may be seen on exposing it in a dark room.

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* The symbol is also much more than the short-hand character, as will be presently apparent.

Name.	Symbol.	Derivation of Name.
Potassium (Kalium.)	K	*Kalium*, from *kali*, Arabic for *ashes*. Manufactories in which certain compounds of potassium and allied sodium salts are made are called *alkali*-works to this day. *Potassium*, from *pot-ash;* so called because obtained by evaporating the lixivium of wood-ashes in pots. From such ashes the element was first obtained, hence the name.
Sodium (Natrium.)	Na	*Natrium*, from *natron*, the old name for certain natural deposits of carbonate of sodium. *Sodium*, from *soda-ash* or *sod-ash*, the residue of the combustion of masses or *sods* of marine plants. These were the sources of the metal.
Ammonium	Am (NH_4)	This body is not an element; but its components exist in all ammoniacal salts, and apparently play the part of such elements as potassium and sodium. Sal ammoniac (chloride of ammonium) was first obtained from near the temple of Jupiter Ammon in Libya; hence the name.
Barium	Ba	From *βαρὺς* (barūs), *heavy*, in allusion to the high specific gravity of "heavy spar," the most common of the barium minerals.
Calcium	Ca	*Calx*, *lime*, the oxide of calcium.
Magnesium	Mg	From *Magnesia*, the name of the town (in Asia Minor) near which the substance now called "native carbonate of magnesia" was first discovered.
Iron (Ferrum.)	Fe	The spelling is from the Saxon *iren*, the pronunciation probably from the kindred Gothic "*iarn;*" the derivation is Aryan; it probably originally meant *metal*.
Aluminium	Al	The metallic basis of alum was at first confounded with that of sulphate of iron, which was the alum of the Romans, and was so called in allusion to its tonic properties, from *alo*, to *nourish*.
Zinc	Zn	From Ger. *zinn*, *tin*, with which zinc seems at first to have been confounded.
Arsenicum	As	*'Αρσενικον* (arsenikon), the Greek name for orpiment, a sulphide of arsenicum. Common white arsenic is an oxide of arsenicum.
Antimony (Stibium.)	Sb	*Στίβι* (stibi), or *στίμμι* (stimmi), was the Greek name for the native sulphide of antimony. The word *antimony* is said to be derived from *ἀντὶ* (anti, *against*), and *moine*, French for *monk*, from the fact that certain monks were poisoned by it.
Copper (Cuprum.)	Cu	From *Cyprus*, the Mediterranean island where this metal was first worked.

Name.	Symbol.	Derivation of Name.
Lead . . . . . . (Plumbum.)	Pb	The Latin word is expressive of "something heavy," and the Saxon *læd* has a similar signification.
Mercury . . . . (Hydrargyrum.)	Hg	*Hydrargyrum*, from *ὕδωρ* (hudōr), *water*, and *ἄργυρος* (arguros), *silver*, in allusion to its liquid and lustrous characters. *Mercury*, after the messenger of the gods, on account of its susceptibility of motion. The old name *quicksilver* also indicates its ready mobility and argentine appearance.
Silver . . . . . (Argentum.)	Ag	*Ἄργυρος* (arguros), *silver*, from *ἀργὸς* (argos), *white*. Words resembling the term *silver* occur in several languages, and indicate a white appearance.

The following are the names of some of the less frequently occurring elements, compounds of which, however, are alluded to in the British and U. S. Pharmacopœias, or met with in pharmacy.

Name.	Symbol.	Derivation of Name.
Bromine	Br	From *βρῶμος* (brōmos), a *stink*. It has an intolerable odor.
Fluorine	Fl	From *fluo, to flow*. Fluoride of calcium, its source, is commonly used as a flux in metallurgic operations.
Boron	B	From *borax*, or *baurak*, the Arabic name of *borax*, the substance from which the element was first obtained.
Silicon	Si	From *silex*, Latin for *flint*, which is nearly all silica (an oxide of silicon).
Lithium	L	From *λίθειος* (litheios), *stony*, in allusion to its supposed existence in the mineral kingdom only.
Strontium . . .	Sr	This name is commemorative of *Strontian*, a mining village in Argyleshire, Scotland, in the neighborhood of which the mineral known as *strontianite* or carbonate of strontium was first found.
Cerium	Ce	Discovered in 1803, and named after the planet *Ceres*, which was discovered on Jan. 1, 1801. The oxalate of cerium is official, but seldom used.
Chromium . . .	Cr	From *χρῶμα* (chrōma), *color*, in allusion to the characteristic appearance of its salts.

Name.	Symbol.	Derivation of Name.
Manganese . . .	Mn	Probably a mere transposition and repetition of most of the letters of the word *magnesia*, with whose compounds those of manganese were confounded till the year 1740.
Cobalt	Co	*Cobalus* or *Kobold* was the name of a demon supposed to inhabit the mines of Germany. The ores of cobalt were formerly troublesome to the German miners, and hence received the name their metallic radical now bears.
Nickel	Ni	*Nickel*, from *nil*, is a popular German term for *worthless*. The mineral now known as nickel ore was formerly called by the Germans *Kupfernickel*, *false copper*, on account of its resemblance to copper (*Kupfer*) ore. When a new metallic element was found in the ore, the name nickel was retained.
Tin (Stannum) .	Sn	Both words are possibly corruptions of the old British word *staen*, or the Saxon word *stan*, a stone. Tin was first discovered in Cornwall, and the ore (an oxide) is called *tinstone* to the present day.
Gold (Aurum) . .	Au	*Aurum* (Latin), from a Hebrew word signifying the color of fire. *Gold.* A similar word is expressive of *bright yellow* in several old languages.
Platinum	Pt	From *platina* (Spanish), diminutive of *plata*, *silver*. It somewhat resembles silver in appearance, but is less white and lustrous.
Bismuth	Bi	Slightly altered from the German *Wismuth*, derived from *Wiesematte*, "a beautiful meadow," a name given to it originally by the old miners in allusion to the prettily variegated tints presented by the freshly exposed surface of this crystalline metal.
Cadmium	Cd	*Καδμεία* (Kadmeia), was the ancient name of calamine (carbonate of zinc), with which carbonate of cadmium was long confounded, the two often occurring together.

Gold, Platinum, Tin, and Silicon are classed with the less important elements, because their salts are seldom used in pharmacy.

It will be noticed that the symbol of an element is simply the first letter of its Latin name, which is generally the same as in the English. Where two names begin with the same letter, the less important has an additional letter added.

QUESTIONS AND EXERCISES.

1. Of how many elements is terrestrial matter composed?
2. In what state do the elements occur in nature?
3. Distinguish between the *art* and the *science* of chemistry.
4. What is the difference between an element and a compound?
5. Enumerate the chief non-metallic elements.
6. Describe a process for the preparation of oxygen.
7. How are gases usually stored?
8. Mention the chief properties of oxygen.
9. What is the source of animal warmth?
10. State the proportion of oxygen in air.
11. Is the proportion constant, and why?
12. Give a method for the elimination of hydrogen from water.
13. State the properties of hydrogen.
14. Why is a mixture of hydrogen and air explosive?
15. Explain the effects producible by the ignition of large quantities of coal-gas and air.
16. What is the nature of combustion?
17. Define a *combustible* and a *supporter of combustion*.
18. Describe the structure of flame.
19. State the principle of the Davy safety-lamp.
20. To what extent is hydrogen lighter than oxygen?
21. What do you mean by *diffusion* of gases?
22. State Graham's law concerning diffusion.
23. Name the source of phosphorus, and give its characters.
24. Why does phosphorus burn in air?
25. What remains when ignited phosphorus has removed all the oxygen from a confined portion of air?
26. Mention the properties of nitrogen.
27. What office is fulfilled by the nitrogen of air?
28. State the proportions of the chief constituents of air.
29. Mention the minor or occasional constituents of air.
30. What is the proportion by weight of nitrogen to oxygen in the atmosphere?
31. Give the specific gravity of nitrogen.
32. How is chlorine prepared?
33. Enumerate the properties of chlorine.
34. Define the terms *deodorizer* and *disinfectant*.
35. Explain the bleaching effect of chlorine.
36. What proportion of hydrogen to chlorine is necessary for the formation of hydrochloric acid gas?
37. State the prominent physical and chemical characters of sulphur.
38. State the prominent characters of carbon.
39. State the prominent characters of iodine.
40. Give the derivations of the names of some of the elements.
41. What are the symbols of oxygen, hydrogen, nitrogen, carbon, chlorine, iodine, sulphur, phosphorus?

THE LEARNER IS RECOMMENDED TO READ THE FOLLOWING PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY CAREFULLY ONCE OR TWICE, THEN TO STUDY (EXPERIMENTALLY, IF POSSIBLE) THE SUCCEEDING PAGES, RETURNING TO AND READING OVER THE GENERAL PRINCIPLES FROM TIME TO TIME UNTIL THEY ARE THOROUGHLY COMPREHENDED.

THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY.

DEFINITION OF CHEMICAL ACTION.

The learner may now proceed to study the manner in which substances act chemically on each other. By acting *chemically* it will be obvious, from the preceding experiments, that what is meant is *so affecting each other that the substances are greatly altered in properties*. A *mixture* of oxygen and hydrogen is still a gas; *a chemical compound* of oxygen and hydrogen is a liquid, namely, water; here is a great alteration in leading properties. Iodine is only slightly soluble in water, and forms a brown-colored solution, and iron is insoluble; but when iodine and iron are *chemically* combined, the product is very soluble in water, forming a light-green solution in which the eye can detect neither iodine nor iron, and which is utterly unlike iron or iodine in any one of their properties. Sand, sugar, and butter rubbed together form *a mere mixture*, from which water would extract the sugar, and ether dissolve out the butter, leaving the sand. Tartaric acid, carbonate of sodium, and water added to each other, form a *chemical compound*, containing neither tartaric acid nor carbonate of sodium, these bodies having attacked each other and formed fresh combinations. These illustrations show that *chemical* action is distinguished from all other actions by (*a*) producing an entire change of properties in the bodies on which it is exerted. Chemical action is further distinguished by (*b*) the fact that it only takes place between definite weights and volumes of matter. This (*a* and *b*) cannot be said of any other action—the action of any of the other great forces of nature (gravitation, heat, light, electricity, etc.); hence the statements (*a* and *b*) furnish a sharp and precise definition of *chemical* action or the chemical force, the force whose manifestations the reader of this book, or of any other manual of chemistry, is studying.

ATOMS.

In a chemical compound, what has become of the constituents? Let the reader place before him specimens of sulphur, iron, and sulphide of iron; or iodine, iron, solid iodide of iron and its solution in water or syrup (*Syrupus Ferri Iodidi*, U. S. P.). In the sulphide of iron what has become of the sulphur and of the iron from which it was made? The *mixture* of sulphur and iron in *combining* to form sulphide of iron has not lost weight, and, indeed, by certain processes it is possible to recover its sulphur as sulphur, and its iron as iron; so that we are compelled to believe, we cannot avoid the conclusion, that sulphide of iron contains particles of sulphur and of iron. But how small must be those particles! Rub a minute fragment to dust in a mortar and place a trace of the powder under the highest power of the best microscope; no yellow particle is visible, not the minutest portion of lustrous metal, but dull-brown miniature fragments of the original mass. The elementary particles of sulphur and iron, or of the elements in any other compound (the chlorine and sodium in common salt or the iodine and iron in solution of iodide of iron), are, in short, too small to be seen. Can they be imagined? Again, no. The mind cannot conceive of a particle of anything (sulphur, iron, sulphide of iron, or what not) so small but what the next instant the imagination has divided it. Yet learner and teacher must have some common platform on which to reason and converse. The difficulty is met by speaking of these inconceivably small particles as *atoms* (ἀτομος, *atomos*, invisible; from the privative *α* and τεμνω, *temnō*, to cut—that which is not cut or divided), an expedient suggested by our countryman Dalton at the commencement of the present century. It is an expedient not perhaps altogether satisfactory, but is the only one possible to the majority of minds in the present state of knowledge and education. We cannot speak of iodine and iron uniting lump to lump, as two bricks are cemented together or blocks of wood glued together, for such is not the kind of action. We cannot select a minute fragment of each to regard as the combining portions, for the minutest fragment we could obtain is visible, and iodide of iron contains neither visible iodine nor visible iron. And yet iodide of iron contains both iodine and iron, or, at least, a given weight of the compound is obtained from the same weight of the constituents, and the same weight of constituents is obtainable from an equal weight of the compound. We might say that molecules are concerned in the operation, but molecules means little masses of—of what? there is positively no word left with which to carry on conversation and description but *atoms*. Any other mode of treating the matter is too subjective for general employment. Moreover, any difficulty in forming a definite conception of an atom is met by regarding an atom, not necessarily as something which *cannot* be divided, but as "a particle of matter which undergoes no further division *in chemical metamorphoses*" (Kekulé). Even physicists regard atoms from much the same point of view; indeed they often speak of still larger portions of matter (molecules) as atoms, meaning thereby "something which is not divided *in certain cases that we are considering*" (Clifford).

THE CHEMICAL FORCE.

What power binds the atoms of a chemical compound together in such marvellous closeness of union that in the couple or group they lose all individuality? Clearly an attractive force of enormous power, a force remotely resembling, perhaps, that which attracts a piece of iron to a magnet. Only by such an assumption can we conceive that common salt contains chlorine and a metal (sodium), or that wood contains carbon, hydrogen, and oxygen. Were not this force thus all-powerful, the carbon in wood would show its blackness and other qualities, and the hydrogen and oxygen give indications of their gaseous and other characters. This attractive force is commonly termed the *chemical force*, sometimes *chemical affinity*. The word *chemism* has also been proposed for it, just as the magnetic force is termed magnetism, but has not been generally adopted.

MOLECULES.

A free, uncombined atom probably cannot exist in a state of isolation, at common temperatures, for any appreciable length of time. For we must regard an atom as the home of an attractive force of great intensity, and the moment such an atom is liberated from a state of combination (say hydrogen from water, or chlorine from salt)—it finds itself in proximity to another atom having similar desires for union, so to speak; the result is an impetuous rushing together and formation of either couples, trios, or groups, according to the nature of the atoms. It would be as difficult to conceive of separate atoms as to imagine that a strong magnet and a piece of steel could be suspended close to each other without being drawn together. It is, doubtless, possible to keep some pairs of atoms apart by the aid of heat, just as the magnet and steel may be parted by a superior amount of force, but such a condition of things is probably abnormal. These pairs and other groups of atoms are conveniently designated by the one word *molecule*, the diminutive of *mole*, a mass; literally little masses. Dissimilar kinds of atoms seem to have greater attraction for each other than similar kinds; for, first, the masses of matter met with in nature in the great majority of cases contain two or more dissimilar elements; and, secondly, at the moment certain elements are liberated from their combination, they are very specially active in combining with other, different, elements; that is to say, the chances are not equal that the liberated elements will either retain their elementary condition or combine to form compounds, but the cases in which compounds are formed are actually in great majority.

RECAPITULATION.

It is desirable that the learner should here make some experiment which will serve to bring again under notice in an applied or concrete form what has just been stated respecting the substances termed *chemical compounds*, and concerning the character of that *chemical force* which resides in the *atoms* of *molecules*. The following will usefully serve this purpose; it is the process for detecting a trace of sulphurous acid in common liquid hydrochloric acid.

As already proved, hydrogen gas and chlorine gas, when united, form hydrochloric acid gas: the latter dissolved in water is the ordinary liquid of the shops termed *Hydrochloric Acid*, the *Acidum Hydrochloricum* or *Muriaticum* of Pharmacopœias. Commercial samples of this liquid not unfrequently contain as an impurity a trace of sulphurous acid gas, a body also already mentioned and experimentally prepared—a trace too small to be detected by its odor. Obtain a specimen of common liquid hydrochloric acid containing as an impurity a trace of sulphurous acid, or adopt the more simple course of purposely adding a few drops of aqueous solution of sulphurous acid (*Acidum Sulphurosum*,* U. S. P.) to some hydrochloric acid. (If no sulphurous acid is at hand, the object may be accomplished by pouring a quarter or half an ounce of liquid hydrochloric acid into a wide-mouthed bottle, then burning a fragment of sulphur on a wire or strip of wood inside the bottle for a few seconds, and shaking the gas and liquid together.) Pour some of the impure liquid hydrochloric acid into a test-tube, add about an equal bulk of water, and then drop in some fragments of the metal zinc. Effervescence will occur, due to the escape of inodorous hydrogen gas, together with a small quantity of a badly-smelling gas, termed sulphuretted hydrogen gas. Bring the mouth of the tube under the nose; the presence of sulphuretted hydrogen will at once be recognized.

The hydrochloric acid has now been *tested* for sulphurous acid. If the experiment be performed on any commercial specimen of the acid, and a smell of sulphuretted hydrogen be observed, the operator will at once be able to state that the specimen contains sulphurous acid as an impurity.

Using Dalton's theory of the atomic constitution of matter, the explanation of what occurs in the successive steps of the foregoing experiment is as follows:—

Hydrochloric acid is a *chemical compound* of hydrogen and chlorine. That it is a chemical compound, and not a mere mechanical mixture of hydrogen and chlorine, is shown by the fact that its properties are altogether different from the properties of its constituents. The attractive power or *chemical force* resident in the *atoms* of chlorine and of hydrogen has caused them to combine in the closest manner imaginable and form pairs of atoms or *molecules* of the chemical compound—hydrochloric acid. Zinc being introduced into the acid, and the atoms of zinc and chlorine having even still greater attraction for each other than the hydrogen for the chlorine, the zinc and chlorine atoms combine and form a new molecule (termed chloride of zinc) which remains in the liquid, while the hydrogen atoms, having the atoms of no other element to combine with if the acid is pure, unite to form pairs, or molecules of hydrogen, and in that state escape from the vessel. If the acid be impure from the presence of sulphurous acid (sulphurous acid gas, it will be remembered, is a compound of sulphur and oxygen), some of the hydrogen atoms, at the moment of their birth, their *nascent* state (from *nascor*, to be born)—the specially active state—finding the atoms of other elements present, namely, the atoms of sulphur and oxygen of the sulphurous acid molecules, combine by preference with these atoms and form new molecules, the sulphur and hydrogen forming sulphuretted hydrogen, and the oxygen and hydrogen producing water: the former escapes with the great bulk of the hydrogen, while the water remains with the water already in the vessels.

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* These aqueous solutions of acids are generally, for the sake of brevity, simply termed acids.

Note.—Ordinary hydrogen gas, that is, hydrogen not in the nascent condition, will not thus attack sulphurous acid. Doubtless the amount, or extent, of attraction of two atoms of hydrogen for one atom of, say, the sulphur in the sulphurous acid molecule is a constant amount, but the uncombined nascent atoms can, it is only fair to suppose, get much nearer to the attacked molecule than they can after they have themselves combined to form a molecule, molecules (but not atoms) having an appreciable amount of space between them, as will be further shown almost immediately. In other words, it is probably distance which prevents an attack which would be inevitable at close quarters. These remarks apply to all similar reactions of other elements.

Conditions and Nature of the Manifestation of the Chemical Force.

The exertion of chemical affinity is only possible when the masses of the bodies touch. Thus it was necessary to bring the oxygen, hydrogen, phosphorus, chlorine, sulphur, carbon, iodine, and iron into ordinary contact, in the respective experiments with those elements, before the various reactions occurred. The exact nature of these actions, as indeed of all in which substances act chemically, would seem to be an interchange, most generally a mutual one, of the atoms of which the molecules consist—a change of partners, so to speak. Thus, in the experiment in which hydrogen and chlorine gases united to form hydrochloric acid gas, a pair of atoms in a hydrogen molecule, and a pair of atoms in a chlorine molecule, finding themselves opposite to each other, change places, the atoms of each of the old molecules unlinking, so to say, and pairing off in fresh couples—as two brothers who for many years have been close companions, and two sisters similarly united, thrown freshly into each other's society, soon accept new and still more congenial couplement.

$$\left\{\begin{matrix}\text{Hydrogen}\\ \text{Hydrogen}\end{matrix}\right\}\text{ and }\left\{\begin{matrix}\text{Chlorine}\\ \text{Chlorine}\end{matrix}\right\}\text{ become }\left\{\begin{matrix}\text{Hydrogen}\\ \text{Chlorine}\end{matrix}\right\}\text{ and }\left\{\begin{matrix}\text{Hydrogen}\\ \text{Chlorine}\end{matrix}\right\}$$

Or, using the symbols of these elements instead of the full names,

$$H\;H \text{ and } Cl\;Cl \text{ become } H\,Cl \text{ and } H\,Cl.$$

Still further economizing space and trouble, the same statement may be made in the following form:—

$$H_2 \text{ and } Cl_2 \text{ become } 2HCl.$$

Once more, by using the *plus* (+) instead of the words "and" or "added to," and the sign or symbol = or *equal* instead of the words "become" or "are equal to," we reach the shortest method of expressing this chemical action:—

$$H_2 + Cl_2 = 2HCl.$$

This is the form in which such an action may be expressed in the student's note-book. It is the shortest and most convenient form, and is instructive and suggestive to the mind.

CHEMICAL NOTATION.

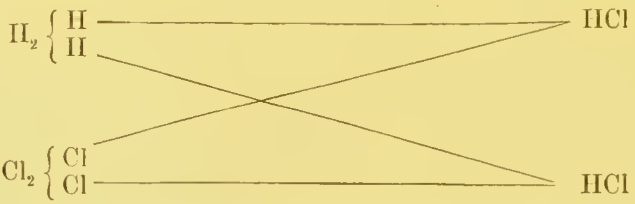
We have thus gradually arrived at a spot in the path of chemical philosophy at which we must halt to more fully discuss the usual method of recording chemical travels. We have arrived at the subject of *chemical notation* (from *noto*, I mark), the art or practice of recording chemical facts by short marks, letters, numbers, or other signs. Already the first capital letter, or the first and one of the following small letters of the Latin names of the elements have been employed as contractions, or short-hand expressions, or *symbols* of the whole *name*. Thus H has been used for the word "hydrogen," and Cl for "chlorine." A *second function* of such a symbol is that of indicating one *atom*. Thus H stands not only for the word or substance "hydrogen," but for one atom of hydrogen. Large and small figures (2 or $_2$) indicate a corresponding number of atoms, the small figure only multiplying the one particular symbol to which it is attached, while a larger figure multiplies all the symbols it precedes. Thus H_2 means two atoms of hydrogen, and Cl_2 two atoms of chlorine; while 2HCl means two atoms of hydrogen and two atoms of chlorine, or, in one word, two molecules of hydrochloric acid gas. A *third function* of such a symbol as H or Cl is that of indicating one *volume* of the element in the gaseous state. Thus H, Cl, and O stand, first, for the substances named hydrogen, chlorine, and oxygen; secondly, for single atoms of hydrogen, chlorine, and oxygen. Thirdly, they represent single and equal volumes of chlorine, hydrogen, and oxygen. It will be remembered that one test-tubeful of hydrogen and an equal sized test-tubeful of chlorine were employed in a previous experiment in forming hydrochloric acid gas, HCl.

The *position* of symbols counts for something. Thus HCl indicates not only the substances hydrogen and chlorine, single atoms of each of the substances, and equal volumes of each, but also that the two substances are *joined together by the chemical force*. If the two letters were placed one under the other, or at some distance apart, or were separated by a comma or a plus sign (+), they would be understood to mean a mere mixture of the elements; but placed as close as the printer's types will conveniently and consistently allow, they must be considered to stand for a compound of the elements, that is to say, hydrochloric acid gas (HCl). The collection of symbols representing a molecule is termed a *formula*. H_2, Cl_2, and HCl are the *formulæ* of hydrogen, chlorine, and hydrochloric acid gas.

$$H_2 + Cl_2 = 2HCl.$$

Such a set of letters, figures, and marks as that on the preceding line is collectively termed an *equation*, because it indicates the equality of the number and nature of the atoms before and after chemical action. On the left hand of the sign of equality are shown two molecules, and on the right hand two molecules; but, of the molecules on the left, one contains two atoms of hydrogen and the other two atoms of chlorine, while of the molecules on the right each contains one atom of hydrogen and one of chlorine. The equation forms a short and convenient plan of recording the facts of experiment.

Instead of an equation, a *diagram* may be employed to exhibit the same fact. Thus:—



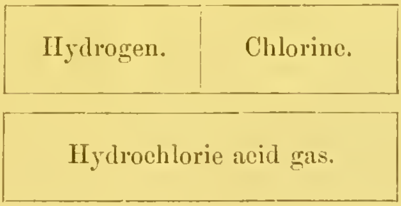
PHYSICAL AND CHEMICAL CONSTITUTION OF MATTER.

Relations of Gases, Liquids, and Solids.

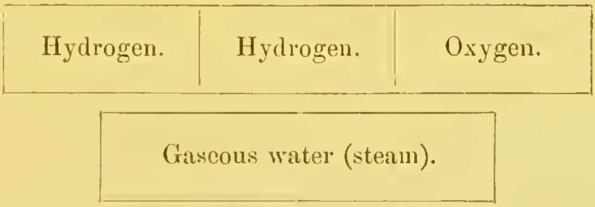
Molecules of gases are not in absolute contact, for a volume of gas may be compressed with very little force to half or one-fourth its bulk—in short, to such an extent that in many cases the molecules sufficiently approximate to form a liquid. In a liquid the molecules are still free to glide about with ease amongst each other; and though in solids they exhibit less mobility, still even solids may be compressed by powerful pressure, so that probably in *no* instance are molecules in absolute contact. (Moreover, from the researches of Caignard de la Tour, and, recently, of Andrews, there would seem to be no sharp lines of demarcation between the gaseous, liquid, and solid conditions of substances.) One's mental picture of the relative position of the molecules of gaseous, vaporous, liquid, or solid matter must be such a picture as that of the moving particles of dust in the air of a room, or such a relation to each other as that of the planets and stars suspended in space. There is abundant experimental evidence to warrant such a conception. A clear transparent fluid appears perfectly homogeneous, but is not so. Its particles are not in contact. Every one who has mixed 5 pints of rectified spirit with 3 pints of water knows that the 100 fluidounces of spirit and 60 fluidounces of water do not when mixed give 160 ounces of "proof" spirit, but only 156 ounces; the molecules of the liquids have gone closer together, having probably a little attraction for each other. Why a gas under pressure should immediately return to its original bulk when the pressure is removed, while a liquefied or solidified gas only slowly resumes the gaseous or vaporous state, is a question which requires for discussion a knowledge of the nature of forces other than the chemical.

For it must be remembered that the study of the chemical force is mainly the study of the internal constitution of molecules, the study of the properties of entire molecules forming the domain of *Physics*—sometimes termed *Natural Philosophy.* (Physics, from φύσις, *phusis*, nature, that is, visible and material nature; the study of actions and reactions which do not involve entire and permanent change in the properties of bodies—the study of the action of heat, light, electricity, magnetism, gravitation, etc., on matter.)

It is necessary, however, to state something more about the physical as well as the chemical conditions of the molecules of a *gas* in order that the learner may be prepared for the fact, that mixtures of certain gaseous elements, in combining to form gaseous compounds, diminish considerably in volume. Thus, while a pint of hydrogen and a pint of chlorine give a quart of hydrochloric acid gas,



two pints of hydrogen and one of oxygen are necessary to produce a quart of gaseous water (steam). It will be remembered that two volumes of hydrogen and one of oxygen were necessary in a previous experiment in which water was formed.



Now, that a pint of hydrogen gas and a pint of chlorine gas should, after chemical reaction or rearrangement of the atoms of the molecules has taken place, form two pints of hydrochloric acid gas, is quite what we should expect. For, first, the reader, by this time, is not astonished that the chemical combination is attended by entire change of properties; and, secondly, the experience of years has led him to expect that a pint of one thing added to a pint of another gives two pints of the mixture. But that two pints of hydrogen and one pint of oxygen should, after combination (and under like conditions of temperature and pressure), give, not three, but two pints of product (steam) is perhaps somewhat astonishing, and needs explanation. To this end let us picture a few of the molecules of hydrogen and as many molecules of chlorine. Draw with a pencil on paper several pairs of crosses (+ +) to represent hydrogen molecules and circles (○○) for chlorine molecules, or, if colored ink is at hand, red pairs of dots for hydrogen and green for chlorine. Or, at once, for facility in printing, let the following pairs of letters *h h* represent a few (say, nine) molecules of hydrogen, and *c c* molecules (nine) of chlorine—before combination.

h h	*h h*	*h h*	*c c*	*c c*	*c c*
h h	*h h*	*h h*	*c c*	*c c*	*c c*
h h	*h h*	*h h*	*c c*	*c c*	*c c*

Then, after combination, we shall have eighteen molecules of hydrochloric acid gas:—

h c	*h c*	*h c*	*h c*	*h c*	*h c*
h c	*h c*	*h c*	*h c*	*h c*	*h c*
h c	*h c*	*h c*	*h c*	*h c*	*h c*

But when two volumes of hydrogen and one of oxygen combine and give two volumes of steam, the mental picture must be not that of molecules somewhat nearer to each other than before, nor any difference in the size of the molecules, but a picture of molecules containing three instead of two atoms—thus, still using pairs of letters, just for the moment, to represent a few (the space will allow only twenty-seven) molecules:—

h h	*h h*	*h h*	*h h*	*h h*	*h h*	*o o*	*o o*	*o o*
h h	*h h*	*h h*	*h h*	*h h*	*h h*	*o o*	*o o*	*o o*
h h	*h h*	*h h*	*h h*	*h h*	*h h*	*o o*	*o o*	*o o*

The twenty-seven molecules (eighteen hydrogen, nine oxygen) will, after combination, become eighteen molecules of steam:

h o h	*h o h*	*h o h*	*h o h*	*h o h*	*h o h*
h o h	*h o h*	*h o h*	*h o h*	*h o h*	*h o h*
h o h	*h o h*	*h o h*	*h o h*	*h o h*	*h o h*

As already suggested, one's mental picture of a number of molecules may well give them such a relation to each other as that of a number of solar systems in the universe, equally distant from each other and each occupying a similar space, yet one system containing a sun and one planet, another a sun and two planets, and so on, or even one or more of the planets having one or more moons. Indeed the atoms in some very complex molecules really appear to have very much the relation to each other of the sun, planets, and moons of a solar system. To indicate such molecules by letters as above would, of course, require more space than is there given to the assumed pictures of molecules.

Here occurs an opportunity that must not be lost of stating a mode of reasoning by which a molecule of oxygen (or of many other elements) is shown to be a double structure—shown to contain two atoms. Five equal-sized bottles are before us, two filled with hydrogen, one with oxygen, and two with steam. (The bottles are hot enough to prevent the steam condensing to water, and all five are at the same temperature.) Apply heat so that all shall be equally heated, *the three different substances expand equally.* Cool equally, *the contents contract equally.* Apply equal pressure to all five, *each is equally affected.* Diminish pressure equally, *each portion of the three substances equally expands.* Gases (practically steam is a gas, it is simply not a permanent gas) thus similarly affected must be, physically, similarly constructed or constituted (a law which will again be referred to, on page 54); each bottle must contain the same number of particles or molecules, and at any one temperature and pressure the molecules in each must be equally distant from each other. We do not know what actual number or distance, but whatever the number and distance it is the same for each bottle. Say that one million is the number, then we shall have a million of molecules in the first hydrogen bottle, a million in the second, a million in the oxygen bottle, and a million in each of the steam bottles. We will cause chemical combination between the two millions of hydrogen molecules and one million of oxygen molecules, producing (as we have seen) two millions of steam molecules, having the properties already stated. But a molecule of steam contains an atom of oxygen. Hence two millions of steam molecules contain two millions of oxygen atoms, which two millions of oxygen atoms have been obtained from one million of oxygen molecules. Therefore each molecule of oxygen was a double structure—each molecule of oxygen contained two atoms of oxygen. As Clifford says, "you cannot put 50 horses into 100 stables, so that there shall be exactly the same amount of horse in each stable; but you can divide 50 *pairs* of horses among 100 stables."

Thus much respecting the constitution of gaseous or vaporous matter. Our knowledge of the constitution of liquid and solid matter is still more limited.

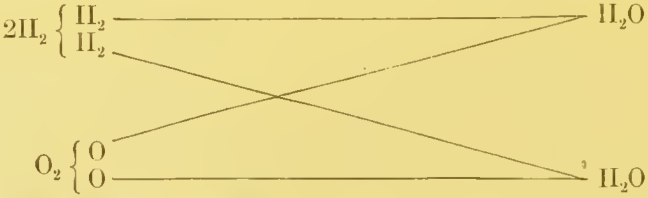
With regard to the notation of the subject, it will be sufficient to state here that while a *symbol* usefully represents one volume of any gas, *a formula of any gas or vapor represents two volumes.* By remembering this general rule we may, by looking at a formula, tell how many volumes of constituents were concerned in the formation of a compound, and therefore what amount of condensation, if any, occurred during the act of formation. By thus reading and interpreting the formula for water, H_2O, we see that two volumes of steam (at any temperature) may be obtained from two volumes of hydrogen and one volume of oxygen (at the same temperature), and thus that the extent of condensation when hydrogen and oxygen (at a stated temperature) unite to form gaseous water (at the same temperature) is from three to two. This subject will again be treated of in connection with those of Chemical Combination and the Specific Gravity of Gases.

Further Remarks on General Chemical Notation.

We may now take an experiment already made as an additional example of chemical action, and describe the simplest way of expressing the same by notation. When two volumes of hydrogen and one of oxygen were caused to combine, the production of flame and noise proved that chemical action of some kind had taken place; had the experiment been performed in dry vessels, evidence of the precise action would have been found in the bedewment or moisture produced by the condensation of the water on the sides of the tube. Similar evidence was afforded on holding a cool glass surface over the hydrogen-flame. The action is expressed in the following equation :—

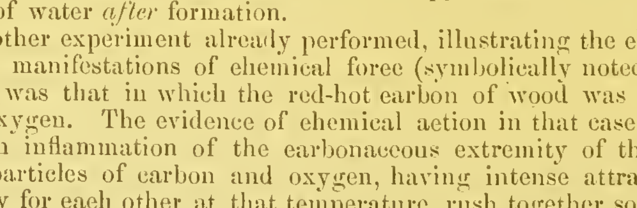
$$2H_2 + O_2 = 2H_2O.$$

Instead of an equation, the following diagram may be employed :—



The foregoing aggregation of symbols or short-hand characters, or *formula*, H_2O, is, then, a convenient picture of the facts that have already come before us, viz., that water is formed of the elements hydrogen, H, and oxygen, O; moreover, that it is formed of two measures or volumes of hydrogen, H_2, to one of oxygen, O; and, thirdly, that the molecule of water (H_2O) is formed of two atoms of hydrogen (H_2) and one of oxygen (O). The formula also fulfils the *fourth function* of indicating that the two volumes of hydrogen and one of oxygen in combining condensed to two volumes of steam. That the resulting bulk of steam afterwards shrunk most considerably in condensing to water is another matter altogether, a physical and not a chemical result, and due to the approximation of the molecules of water *after* formation.

Another experiment already performed, illustrating the character of the manifestations of chemical force (symbolically noted as follows), was that in which the red-hot carbon of wood was plunged into oxygen. The evidence of chemical action in that case was the sudden inflammation of the carbonaceous extremity of the wood. The particles of carbon and oxygen, having intense attraction or affinity for each other at that temperature, rush together so impetuously as suddenly to produce a large additional quantity of heat, an amount sufficient to cause the particles to emit an intense white light. The action between carbon and oxygen is expressed on paper in either of the following ways :—



CO_2 is the formula of the well-known gaseous body commonly termed carbonic acid gas.

The reader should here draw for himself equations or diagrams similar to those on page 46, and thus show the formation of the three bodies he has already produced—namely, phosphoric anhydride (P_2O_5), sulphurous acid gas (SO_2), and iodide of iron (FeI_2), submitting the same, if possible, to a tutor or other authority to assure himself of their correctness.

Note.—In the foregoing experiments several illustrations occur of the formation of compounds having the gaseous, liquid, and solid conditions, in one of which three forms all matter in the universe apparently exists.

LAWS OF CHEMICAL COMBINATION (BY WEIGHT).

Chemistry as a science is little more than a hundred years old, though very many of the facts and operations we now term chemical have been known as isolated items of knowledge for centuries. Thus, the ancient Egyptians made glass, vitriol, soap, and vinegar; and the Greeks started the idea that matter was composed of a few elements, imagining earth, air, fire, and water to be elements. But the great general principles which interlace and bind together separate facts, those which from their extensive application and importance are denominated *laws*, have all been brought to light since the year 1770.

First Law relating to Chemical Combinations.

Between 1785 and 1800, Bryan Higgins, William Higgins, Wenzel Richter, and Proust made analyses and researches which led up to the following generalizations: *When compounds unite to form definite chemical substances, they always combine in the same proportions.* The curious character of this fact could but be most striking, and indeed is so now, to the mind receiving it for the first time. Thus water (a compound) added to quicklime (a compound) gives slaked lime, a perfectly definite chemical substance. But whereas sand and water, sugar and water, sand and sugar, and such *mixtures* may be obtained by adding together the ingredients in any proportions whatever, say 90 of sugar and 10 of sand, or 10 of sugar and 90 of sand, slaked lime (say 100 parts) invariably results from the combination of 75¾ of quicklime and 24¼ of water. If a larger proportion than 75¾ per cent. of quicklime be employed, the excess remains as quicklime mixed with the slaked lime; and if more than 24¼ per cent. of water be used, an excess of water remains with the slaked lime and evaporates if the mixture be exposed to the air. Dalton discovered that when *elements* unite to form a definite substance, they, like compounds, always combine in the same proportions; and he was the first to set forth the law in a manner which was at once clear and comprehensive enough to include the former generalization. Thus:—

A definite compound always contains the same elements in the same proportions.

Take another example. Common salt always contains 39⅓ per cent. of the metal sodium to 60⅔ of chlorine, and water always 89 of oxygen and 11 per cent. of hydrogen (more exactly 88.89 to 11.11). As with quicklime and water, so with the chlorine and sodium, and the constituents of many (not all) chemical compounds; in such cases if either be added to the other in any quantity beyond stated proportions, the excess plays no part whatever in the act of combination. (In *some* cases, as will be seen directly, excess of either plays a very simple but very remarkable part.) In short, whether a compound be made directly from its elements, or by the combination of other compounds, or indirectly as one of two products of the action of substances chemically on each other, whatever be its origin, if it is a definite compound it always contains the same elements in the same proportions.

Second Law relating to Chemical Combinations.

Dalton further made such experimental researches as enabled him to lay down a second great law. He found that, while many substances only united chemically in one proportion, others combined in two or even more, and he studied several such naturally related bodies. He found that while carbonic oxide (a gas formed when charcoal is burned with an insufficient supply of air) contains such a proportional weight of carbon and oxygen as is represented by (to use the simplest figures) 3 and 4, carbonic acid (a gas formed when charcoal is burned with excess of air) contains 3 of carbon to exactly twice 4 of oxygen. He proved that a similar relation existed between two compounds of carbon and hydrogen, and between a cluster of compounds of nitrogen and oxygen. The first of the latter, to a given quantity of nitrogen, contains a certain proportion of oxygen; the next, to the same quantity of nitrogen, has exactly twice the proportion of oxygen: and the others have exactly three, four, and five times as much oxygen as the first, the quantity of nitrogen remaining the same throughout. Dalton thus generalized these facts:—

When two elements unite in more than one proportion, the resulting compounds contain, to a constant proportion of one element, simple multiple proportions of the other—or the weights of the constituent elements bear some similar simple relations to each other.

Thus carbonic oxide gas is a definite compound always containing fixed proportions of carbon and oxygen, and carbonic acid gas is also a definite compound always containing fixed proportions of carbon and oxygen. Both thus obey the first law of combination. But whereas carbonic oxide contains, or may be made from, 30 parts (ounces, grains, or other weights) of carbon and 40 of oxygen, carbonic acid contains, or may be made from, 30 parts of carbon and exactly twice 40 of oxygen.

This second law cannot but be as striking as the first when freshly unveiled to the mind. Sand and sugar, or any substances which do not act *chemically* on each other, may be mixed in the proportions of 30 to 40, 30 to 80, 30 to 60, or any other quantities; but if an attempt be made to burn 30 parts of carbon in 60 of oxygen, the elements will themselves naturally assert their own special combining powers, and refuse, so to say, to unite in these proportions: the 30 of carbon will first combine with 40 of oxygen and form 70 of carbonic oxide, and this gas, which, had it the opportunity, would combine with 40 more of oxygen and form carbonic acid gas, finding only half that quantity, namely, 20, of oxygen present, contents itself by one-half (that is, 35 of carbonic oxide), accepting the 20 of oxygen and becoming carbonic acid gas, while the other half remains as carbonic oxide. This is a most wonderful fact. Again, if 30 parts of carbon be burnt in more than 80, say 85, of oxygen, only 80 will be used, the other 5 remaining as oxygen merely *mixed* with the resulting carbonic acid gas. If we attempt to burn 30 parts of carbon in less than 40 of oxygen, the oxygen will take up three-fourths its weight of carbon and form carbonic oxide, while the excess of carbon will remain as carbon.

Recapitulation.

Nature does not always permit man to mix things in any proportions he pleases. She does sometimes. She does if he only stirs things together, or if he only uses the attractions of adhesion or cohesion in binding the materials together; but if he employs chemical attraction, she restricts him to special proportions. That is to say, if the things mixed do not attack one another or intimately combine, then admixture may be effected in any proportion; and the mixture is a mere mixture having the mean properties of its components. Examples of such mixtures are seen in compound plasters, pill-masses, confections, and plum-puddings. But if the things do unite to form, not a mere mixture having the mean properties of its components, but a compound having new and distinct and definite characters of its own, then nature does not permit man to mix the things in any proportion he pleases. The proportion is one fixed and constant; and if he substitutes proportions of his own, the things unite in the proportions fixed by nature, and the excess he has added either remains in its original uncombined condition, or it combines with the compound already produced to form a second *different* compound. Any one compound, that is, the *same* compound, always contains the same elements in the same proportions, and can only be made from the same elements in the same proportions. An attempt to mix the same elements in other proportions would result in one of two failures, namely, either the extra proportion would remain free and uncombined, or it would combine and convert the first compound, or a portion of it, into a *different* compound. The fresh compound thus produced, like the first, and indeed like all definite compounds, of course always contains the same elements in the same proportions.

In short (law 1) any definite compound always contains the same elements in the same proportions, and (law 2) any two elements uniting in more than one proportion unite in multiples of that proportion, and produce so many different definite compounds. Taking hydrogen as uniting in proportions of 1, oxygen unites in proportions of 16—that is, 16, twice 16, thrice 16, and so on, never in intermediate proportions. Carbon unites in proportions of 12, sulphur of 32, chlorine of 35½. And every other element has its combining proportion fixed by nature.

The student of chemistry is recommended to accept these two great natural facts, great enough to be dignified by the name of *laws*, in all their inherent solidity and simplicity. Of course, he will wonder *why* substances should combine, chemically, only in fixed proportions when forming a definite body, and *why*, when a substance combines in more than one proportion to form different compound bodies, the proportions should only be multiple proportions; and an extremely ingenious and useful explanation has been suggested by Dalton (see the following paragraphs on the theory that matter is built up of atoms); but man has not yet succeeded in so questioning nature as to gain from her a *satisfactory* answer to such questions; hence, until he does succeed, any hypothesis, such as Dalton's, should be held intelligently but loosely. The facts themselves, however, should be grasped with the student's utmost tenacity.

Third Law relating to Chemical Combination.

Careful consideration of the foregoing two great laws has suggested an important truth sometimes termed *The Law of Chemical Combination*, namely: *The proportions in which two elements unite with a third are the proportions (or simple multiples or submultiples of the proportions) in which they unite with each other.* Thus oxygen in proportions of 16 unites with hydrogen, and carbon in proportions of 12 unites with hydrogen; therefore 16 and 12 are the proportions in which oxygen and carbon will unite with each other.*

THE ATOMIC THEORY.

The laws which Dalton (1803 to 1808) so largely aided to unveil —two grand and wonderful truths—he explained and correlated by a simple and beautiful hypothesis. *Dalton suggested that matter was not infinitely divisible, but composed of minute particles or* ATOMS *having an invariable character.* In the words of Wurtz, "*To an old and vague notion he attached an exact meaning by supposing that the atoms of each kind of matter possess a constant weight, and that combination between two kinds of matter takes place not by penetration of their substance, but by juxtaposition of their atoms.*"

Thus under this hypothesis, or atomic theory as it is generally termed, carbonic oxide is a definite compound always containing the same elements in the same proportions, *because* each particle of it is composed of an atom of carbon and an atom of oxygen chemically united, the weights of the atoms being in the proportion of 3 and 4, that is, having a constant weight of 12 and 16, as we now believe. Carbonic acid gas is also a definite compound always containing the same elements in the same proportions, and the proportion of oxygen is just double that in carbonic oxide, *because* each particle of it is composed of an atom of carbon (weighing 12) and two atoms of oxygen (each weighing 16).

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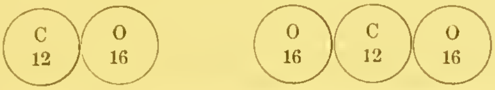
* See Axiom 1 in Hawtrey's fascinating "Introduction to the Elements of Euclid," Longmans & Co., London, 2*s*. 6*d*., a book strongly recommended to any chemical student who is not familiar with the mode of reasoning commonly termed geometrical.



Imaginary pictures of molecules of carbonic oxide gas and carbonic acid gas.*

Again, the facts that with 12 of carbon oxygen unites in the proportion of 16, or a multiple of 16; that with 12 of carbon sulphur unites in the proportion of 32, or a multiple of 32 (the liquid known as disulphide of carbon is a chemical compound of 12 of carbon to twice 32 of sulphur); and, thirdly, that oxygen and sulphur unite in proportions of 16 and 32, are at once explained on the assumption that these elements exist in atoms which have the respective weights mentioned. Existing in indivisible particles (atoms) which weigh 16, 12, and 32, oxygen, carbon, and sulphur *must* unite in indivisible weights of 16, 12, and 32.

ATOMIC WEIGHTS.

What has just been stated respecting two or three elements is true of all the elements. It is a fact, that, when elements unite with one another in the peculiar and intimate manner termed chemical, they do not combine in the haphazard proportions of a mere mixture, but in one fixed and constant proportion. Such proportions or weights represent, according to Dalton, the weights of their atoms. Oxygen unites with other elements in proportions of 16, therefore 16 is the weight of the atom of oxygen. Chlorine unites with other elements in proportions of 35½, therefore 35½ is the atomic weight of chlorine. And for a similar reason the atomic weights of hydrogen will be 1, carbon 12, sulphur 32, nitrogen 14, and iodine 127. Of course it will be understood that these are the *relative* weights of atoms, for we cannot know the absolute weights. All that is known is that the chlorine atom, for instance, is 35.5 times as heavy as the hydrogen atom, whatever the absolute weight of the latter may be, and the iodine atom 127 times as heavy. The quantity of metal which with 35.5 of chlorine will form a chloride, and with twice 35.5 a second chloride (dichloride or bichloride), will require 127 of iodine to form an iodide, and twice 127 of iodine to form a second iodide (a diniodide or biniodide).*

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* The size of atoms, their shape, their absolute weight—whether or not they are in actual contact—whether or not they are fixed in relation to each other, free to move about each other, or in a constant state of motion—and whether or not the chemical force actuates them as the force of gravitation influences our earth, and moon, and solar systems, are matters of which at present we know almost nothing. The two pictures are not intended to convey any impression that the following formulæ do not give: CO or OC, OCO or OOC or COO or CO_2.

Note on Notation.—A *fourth function* of a symbol is to represent atomic *weight*. Thus the symbols H, Cl, O, etc., not only perform the office of representing (*a*) names, (*b*) single volumes, and (*c*) single atoms, but (*d*) definite weights of the respective elements.

$$H = 1,\ Cl = 35.5,\ O = 16,\ I = 127,\ N = 14,\ K = 39, \text{ etc.}$$

LAWS OF CHEMICAL COMBINATION (BY VOLUME).

In 1809 Gay-Lussac showed it to be a fact that when gaseous elements unite with one another in the intimate manner termed chemical, they do not combine in the haphazard proportions (that is, proportions by measure or volume) of a mere mixture, but in constant proportions in the case of any single definite compound, and in simple multiple proportions in cases where two elements form more than one definite compound. He thus proved that the laws respecting the constancy of weight with which elements combine hold good with reference to volume, at all events in those cases in which elements exist in or can be made to assume the gaseous condition. A volume of hydrogen gas and an equal one of chlorine gas give hydrochloric acid gas. Two volumes of hydrogen and one of oxygen give water-vapor or steam. Such volumes or simple multiples are alone the proportions by bulk in which elements combine. If any excess of either gas be mixed and combination attempted, only the stated proportions really combine, the excess remaining unaltered. Further, following Gay-Lussac, on weighing these similar and equal volumes of hydrogen, chlorine, and oxygen, we find that the chlorine is 35.5 times as heavy as hydrogen, and oxygen 16 times as heavy as hydrogen.

In 1811 and 1814, Avogadro and Ampère, reasoning on the fact that all gases are similarly affected by variations of pressure (Boyle, 1662, verified by Mariotte) and temperature (Charles), concluded that all gases must be similarly constituted—similarity in properties always indicating similarity in character or nature; in other words, that, if *equal volumes of gases* be taken *under like conditions*, each will *contain the same number of molecules*, similar in *size* and equally distant apart. The deduction is obvious. *The weights of molecules of gaseous elements* (*that is, pairs of atoms, and therefore of atoms themselves*) *must differ to the extent that the weights of equal volumes of those elements differ.* Equal volumes of hydrogen, chlorine, and oxygen, weighing respectively 1, 35.5, and 16, and each of these volumes containing an equal number of molecules, each formed of two atoms, it follows that the relative weights of the atoms will be 1, 35.5, and 16.

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* Only the atomic weights of the above and a few of the chief metallic elements need be committed to memory; others can be sought out as occasion may require. A complete Table of *combining proportions* of elements, or Atomic Weights, is given at the end of the volume.

It will thus be seen that the weight of the *volume* in which an element combines, and the *actual weight* in which it combines, irrespective of volume, are identical. For instance, we should find by experiment that, as a simple matter of fact, oxygen unites with other elements in proportions of 16 by weight, while hydrogen combines in proportions of 1. Turning, then, to experiments on the volumes in which hydrogen or oxygen combine, and having ascertained those volumes, and then having weighed them, we should find that the oxygen volume weighs 16, while the hydrogen weighs 1. In compounds in which hydrogen was found in proportions of 1 grain, oxygen would be found in proportions of 16 grains. In gaseous compounds in which hydrogen was found in proportions of, say, 27 ounces by measure, oxygen would be found in proportions of 27 ounces by measure; the 27 ounces of hydrogen would be found to weigh 1 grain, and the 27 ounces of oxygen to weigh 16 grains.

Thus the two great facts or laws respecting chemical compounds which Dalton laid down by ascertaining the exact weights in which bodies combine, Gay-Lussac confirmed by experiments on the exact volumes in which elements combine. Further, Gay-Lussac's experiments and Avogadro's reasoning strongly supported Dalton's theory of atoms.

RECAPITULATION.

What are atomic weights or combining weights? First, they are represented by the smallest proportion (relative to 1 part of hydrogen) in which an element migrates from compound to compound. Thus 1 part by weight of hydrogen can be eliminated from 18 similar parts of water by action of certain metals, leaving 1 of hydrogen and 16 of oxygen combined with the metal. From the latter compound 1 more of hydrogen is eliminated by a second experiment with more metal, leaving 16 of oxygen combined with the metal. In these and other well-known reactions 16 parts of oxygen take part in the various operations; 16, therefore, is the probable atomic weight of oxygen; and so with other elements and radicals. Secondly, the weights of the atoms, or the atomic weights, of the gaseous elements already studied, must differ from each other to the extent that equal volumes of those elements differ in weight. For equal volumes of an element contain an equal number of molecules equal in size (Avogadro's and Ampère's conclusion), and each molecule is composed of two atoms; so that equal volumes of elements contain an equal number of atoms. Now, bulk for bulk, chlorine is thirty-five and a half (35.5) times as heavy as hydrogen; so that the molecule of chlorine must be 35.5 times the weight of the molecule of hydrogen; for molecules are equal in bulk. And as the molecules of chlorine and hydrogen contain two atoms each, the atom of chlorine must be 35.5 times as heavy as that of hydrogen. The actual weight of atoms can never be ascertained, but that is of little consequence if we can only determine, with exactitude, their comparative weights. Comparing, then, all atomic weights, sometimes obscurely termed equivalents, with each other, and selecting hydrogen as the standard of comparison (because it is the lightest body known, and therefore, probably, will have the smallest atomic weight), and assigning to it the number 1, we see that the atomic weight of chlorine will be represented by the number 35.5. By parity of reasoning the atomic weight of oxygen is 16; for oxygen is found, by experiment, to be 16 times as heavy as hydrogen. Similarly the atomic weight of nitrogen is found to be 14. The atomic weight of carbon is 12—not because its vapor has been proved to be 12 times as heavy as hydrogen, for it has never yet been converted into the gaseous state, but because no gaseous compound of carbon, which has been analyzed, has been found to contain in 2 volumes (one of which, if hydrogen, would weigh 1 part) less than 12 parts of carbon.

By thus weighing equal volumes of gaseous elements, or equal volumes of gaseous compounds of non-volatile elements, and ascertaining by analysis the proportion of the non-volatile element whose atomic weight is being sought to the volatile element whose atomic weight is known, the atomic weights of a large number of the elements have been determined. Some of the elements, however, do not form volatile compounds of any kind; the stated atomic weights of these elements, therefore, are at present simply the proportions by weight in which they combine with or displace elements whose atomic weights have been determined, the proportion being in most cases checked by isomorphic considerations and the relation of the element to other forces, especially heat.* (*Vide infra.*)

MOLECULAR WEIGHT AND MOLECULAR VOLUME.

The weight of the molecule is simply the sum of the weights of its atoms; thus

$$H_2 = 2;\ O_2 = 32;\ Cl_2 = 71;\ H_2O = 18;\ HCl = 36.5.$$

Molecular Volume.—If the quantities just mentioned be weighed out (in grains or other weights), or if the molecular weight of any gases or liquids be taken and exposed to similar (high) temperatures and pressures, *they will all be found to occupy the same volume.* Conversely, if equal volumes of gases or vapors be measured out, and then the whole weighed, the resulting figures (all referred to 2 of hydrogen as a starting-point or standard) are the molecular weights of the respective substances. Thus a volume of hydrogen (about half a gallon) which, at a temperature of, say, 300° F. or 400° F., and common atmospheric pressure, would weigh 2 grains, would in the case of vapor of water (steam) weigh 18 grains. Hence we are justified in considering, indeed compelled to consider, the molecule of water to contain two atoms of hydrogen (= 2) and one of oxygen (= 16), and its formula to be H_2O (= 18), and not H_4O_2, in which case its vapor would be twice as heavy as it really is found to be.

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* *Isomorphous* bodies (from ἴσος, *isos*, equal, and μορφή, *morphē*, form) are those which are similar in the shape of their crystals. The identity in crystalline form is so commonly associated with similarity of constitution that non-crystalline substances resembling each other in structure are often regarded as isomorphous. When one element unites with another in more than one proportion, and its atomic weight is so far uncertain, the isomorphism of either of its compounds with some other compound of known constitution is usually accepted as decisive evidence as to which proportion is atomic. The specific heat of elements will be treated of subsequently.

Construction of Formulæ.—The composition of hydrochloric acid (HCl), water (H_2O), ammonia (NH_3), carbonic acid gas (CO_2), or any other compound, as well as the weight of an element that may be concerned in its formation, cannot be ascertained by actual experiment until the student is far advanced in practical chemistry—until he is able to *analyze* not only *qualitatively*, but, by help of a balance, *quantitatively*. The percentage composition of a substance having been determined by quantitative analysis, its formula is constructed by aid of the foregoing and other theoretical considerations. The correctness of such formulæ can be verified by expert analysts, but must be taken for granted by learners. This subject will again be referred to in the latter part of this Manual.

QUANTIVALENCE OF ATOMS.

Turning from the *weights* of atoms, their *value* may now be considered; their *quantivalence* (from *quantitas*, quantity, and *valens*, being worth) may be stated. The chemical value of atoms in relation to each other may be compared to the exchangeable value of coins. As compared with a penny (1*d.*) a groat (4*d.*) is four-valued; as compared with hydrogen carbon is quadrivalent. Here again hydrogen is conveniently adopted as the standard of comparison. An atom of oxygen in its relations to an atom of hydrogen is bivalent (pronounced thus, biv′-a-lent; of double worth, from *bis*, twice, and *valens*): an atom of it will displace two atoms of hydrogen, or combine with the same number; nitrogen is usually trivalent (triv′-a-lent; from *tres*, three, and *valens*); and carbon, quad-riv′-a-lent (from *quatuor*, four, or *quater*, four times, and *valens*). Chlorine, iodine, and bromine, as well as potassium, sodium, and silver among the metals, are, like hydrogen, univalent (u-niv′-a-lent; from *unus*, one, and *valens*). Barium, strontium, calcium, magnesium, zinc, cadmium, mercury, and copper, like oxygen, are bivalent. Phosphorus, arsenicum, antimony, and bismuth, like nitrogen, usually exhibit trivalent properties; but the composition of certain compounds of these five elements shows that the several atoms are sometimes quinquivalent (quin-quiv′-a-lent; *quinquies*, five times, and *valens*). Gold and boron are trivalent. Silicon (the characteristic element of flint and sand), tin, aluminium, platinum, and lead resemble carbon in being quadrivalent. Sulphur, chromium, manganese, iron, cobalt, and nickel are sexivalent (sex-iv′-a-lent; from *sex*, six, or *sexies*, six times, and *valens*), but frequently exert only bivalent, trivalent, or quadrivalent activity. This *quantivalence* (quant-iv′-a-lence; from *quantitas*, quantity, and *valens*), also termed *atomicity* (maximum quantivalence), *dynamicity*, and *equivalence* of elements, may be ascertained at any time on referring to the table of the Elements at the end of this volume, where

Roman numerals, i, ii, iii, iv, v, vi, are attached to the symbols of each element to indicate atomic univalence, bivalence, trivalence, quadrivalence, quinquivalence, or sexivalence. Dashes (H', O'', N''') similar to those used in accentuating words are often used instead of figures in expressing quantivalence. The quantivalence of elements, as they one after another come under notice, should be carefully committed to memory; for the composition of compounds can often be thereby predicated with accuracy and remembered with ease. For instance, the hydrogen compounds of chlorine, Cl', oxygen, O'', nitrogen, N''', and carbon, C'''', will be respectively $H'Cl'$, H'_2O'', H'_3N''', and H'_4C'''',—one univalent atom, H', balancing or saturating one univalent atom, Cl'; two univalent atoms, H'_2, and one bivalent atom, O'', saturating each other; three univalent atoms, H'_3, and one atom having trivalent activity, N''', saturating each other; and four univalent atoms, H'_4, and one quadrivalent atom, C'''', saturating each other. Carbonic acid gas, $C^{iv}O^{ii}_2$, again, is a saturated molecule containing one quadrivalent and two bivalent atoms.

The subject of quantivalence will be further explained after the first six metals have been studied, when abundant illustrations of it will have occurred.

DEFINITIONS.

Chemistry is the study of the chemical force.

The Chemical Force, like other forces, cannot be described, for, like them, it is only known by its effects. It is distinguished from other forces by the facts that (*a*) it produces an entire change of properties in the bodies on which it is exerted, and (*b*) that it is exerted only between definite weights and volumes of matter. Like the *force of cohesion*, which is the name given to the attraction which molecules have for each other, and which is great in solids, small in liquids, and apparently absent in gases, and like the *force of adhesion*, which is the name given to the attraction which a mass of molecules has for another mass, *the chemical force* acts only within immeasurable distances: indeed, inasmuch as the chemical force appears to reside in atoms, that is to say, is exerted inside a molecule, while all other forces affect entire molecules, the chemical force may be said to be distinguished (*c*) by being exerted within a smaller distance than that at which any other force is exerted.

An Element is a substance which cannot by any known means be resolved into any simpler form of matter.

An Atom of any element is a particle so small that it undergoes no further subdivision in chemical transformations.

A Molecule is the smallest particle of matter that can exist in a free state.

A mere Mixture of substances is one in which each ingredient retains its properties.

A Chemical Compound is one in which definite weights of constituents have combined, and during combination have undergone an entire change of properties. A "compound" in pharmacy is an intimate mixture of substances, but still only a mixture; it is not a *chemical* compound, the ingredients have not entered into *chemical* union or combination.

Combustion is a variety of chemical combination, a variety in which the chemical union is sufficiently intense to produce heat and, generally, light.

The Law of Diffusion is one under which gases mix with each other at a rate which is in inverse proportion to the square root of their relative weights; that is, irrespective of and even in spite of their comparative lightness or heaviness.

A Chemical Symbol is a capital letter, or a capital and one small letter. It has four functions, namely:—

1. It is short-hand for the *name* of the element.
2. It represents one *atom* of the element.
3. It stands for a constant *weight* of the element—the atomic weight or combining weight.
4. Symbols represent single and equal *volumes* of gaseous elements.

A Chemical Formula represents *a molecule* either of an element or of a compound. It has four other functions:—

1. It indicates at a glance the *names* of the elements in the molecule.
2. Its symbol or symbols, together with a small figure attached to the foot of any symbol, show the *number of atoms* in the molecule.
3. It stands for a constant weight of a compound—the molecular weight—the sum of the combining *weights* or of the weights of the atoms in the molecule.
4. It represents *two volumes* of the substance, if volatilizable, in the state of gas or vapor, and the number of volumes of gaseous elements from which two volumes of any gaseous compound were obtained.

A Chemical Equation or *a Chemical Diagram* is a collection of formulæ and symbols so placed on paper as to form a picture or illustration of the state of things before and after that metathesis (interchange of atoms) of molecules which results in the formation of molecules of new substances.

A Solid is a substance the molecules of which are more or less immobile, though probably not in absolute contact.

A Liquid is a substance the molecules of which so freely move about each other that it readily assumes and retains the form of any vessel in which it is placed.

A Gas is a substance the molecules of which are so far apart that they seem to have lost all attraction for each other, and, indeed, to have acquired the property of repulsion to such an extent that they are only prevented from receding to a still greater extent by the pressure of surrounding matter. Motion is especially characteristic of gaseous fluids.

The Three Laws regulating Chemical Combination (either by weight or volume).

First. A definite compound always contains the same elements and the same proportions of those elements—by weight or volume.

Second. When two elements unite in more than one proportion, they do so in simple multiples of that proportion.

Third. The proportions in which two elements unite with a third are the proportions in which they unite with each other.

Atomic Weights are, first, the proportions in which elements are found to combine with each other by weight. (The figures showing these proportions are purely relative, but all chemists agree to make this relation fixed by giving the number 1 to hydrogen.) Secondly, they are the weights of equal volumes of elements in the state of gas (relative to 1 of hydrogen).

Molecular Weights.—These are the weights of equal volumes of gases or vapors, under equal circumstances of temperature and pressure, and relative not to 1 but to 2 of hydrogen. In the case of non-volatile bodies, molecular weight is deduced from the observed analogies of the bodies with those whose molecular weight admits of proof. The molecular weight of a compound is the sum of the atomic weights.

Quantivalence of Atoms.—The observed power, force, or value for work of an atom—relative to 1 of hydrogen.

THE LEARNER IS RECOMMENDED TO READ THE FOREGOING PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY CAREFULLY ONCE OR TWICE, THEN TO STUDY (EXPERIMENTALLY, IF POSSIBLE) THE FOLLOWING PAGES, RETURNING TO AND READING OVER THE GENERAL PRINCIPLES FROM TIME TO TIME UNTIL THEY ARE THOROUGHLY COMPREHENDED.

Minor Principles and Generalizations will be found scattered throughout the following pages.

Students of pure chemistry, especially when fairly well acquainted with chemical facts, will also find the Principles of Chemistry, including the probable Constitution as distinguished from the mere Composition of Chemical Substances, amply set forth in Tilden's "Chemical Philosophy," one of Longman's series of "Text-books of Science."

QUESTIONS AND EXERCISES.

42. What do you understand by *chemical* action? Give examples.

43. How is chemical force distinguished from other forces?

44. Adduce evidence that elements exist in compounds; that sulphide of iron, for instance, still contains particles of sulphur and iron, though it possesses properties so different from those elements.

45. Define the term atom.

46. What condition is essential for the manifestations of chemical force?

47. Can an atom exist in an uncombined state? and when are the atoms of an element most potent to enter into chemical combination?

48. What is a molecule?

49. How may the results of chemical reactions be expressed on paper?

50. Enumerate the functions of a symbol.

51. Give the additional functions of a chemical formula.

52. Describe by a diagram or an equation the reaction which ensues when red-hot charcoal is plunged into oxygen gas.

53. Draw diagrams representing the formation of P_2O_5, SO_2, and FeI_2 respectively.

54. Enumerate the differences in the physical conditions of the molecules in a solid, a liquid, and a gas.

55. State the law of constant proportions.

56. State the law of multiple proportions.

57. State the law of reciprocal proportions.

58. Give illustrations of the above laws.

59. Describe the origin and use of the atomic theory.

60. What do you understand by the atomic weight, and the molecular weight of an element?

61. Representing the weight of an atom of hydrogen as 1, what will be the atomic weights of carbon, sulphur, nitrogen, and iodine? Give reasons for considering the stated weights to be correct.

62. In what proportion, by volume, do elements in the gaseous state chemically combine?

63. What relation exists between the combining volumes of elements in the gaseous state and their atomic weights? Give the explanation for this.

64. Is there any difference between the molecular volume of a simple or of a compound gas?

65. Define isomorphism.

66. Explain the value of isomorphism as evidence of atomic weight.

67. What is to be understood by the quantivalence of an element? Give examples of univalent, bivalent, trivalent, and quadrivalent atoms.

68. How may the quantivalence of an element be expressed in its atomic symbol?

69. Give the formulæ of two or three compounds in which the quantivalence of one atom is saturated by the combined quantivalence of others.

The reader is also recommended to question himself, or be questioned, on the "definitions" given on pages 56, 57, and 58.

THE ELEMENTS AND THEIR COMPOUNDS.

Having thus obtained a general idea of the nature of such elements as have especial interest for the medical and pharmaceutical student, and which indeed are all with which any student of chemistry should at present occupy his attention, we may pass on to consider in detail the relations of the elements to each other. The elements themselves, in the free condition, are seldom used in medicine, being nearly always associated—bound together by the chemical force; in this combined condition, therefore, they must be studied. Each combination of elements or chemical compound will, in the following pages, be regarded as containing two parts or roots, two radicals; the one usually metallic, or, to speak more generally, basylous; the other commonly a non-metallic, simple or complex, acidulous radical. The basylous radicals, or metals, will be considered first, the acidulous radicals afterwards. Each radical will be studied from two points of view, the synthetical and the analytical: that is to say, the properties of an element on which the preparation of its compounds depends will be illustrated by descriptions of actual experiments, and thus the principles of chemistry, and their application to medicine and pharmacy, be simultaneously learnt; then the reactions by which the element is detected, though combined with other substances, will be performed, and so the student will be instructed in qualitative analysis. Synthetical and analytical reactions are, in truth, frequently identical, the object with which they are performed giving them synthetical interest on the one hand, or analytical interest on the other.

A good knowledge of chemistry may be acquired synthetically by preparing considerable quantities of the salts of the different metals, or analytically by going through a course of pure qualitative analysis. But the former plan demands a larger expenditure of time than most students have to spare, while under the latter system they generally lose sight of the synthetical interest which attaches to analytical reactions. Hence the more useful system, now offered, of studying each metal, etc., from both points of view, time being economized by the operator preparing only small specimens of compounds.

Chemical synthesis and analysis, thoughtfully and conscientiously followed, without hurry and mere superficial consideration, but, of course, without undue expenditure of time, will insensibly carry the principles of chemistry into the mind, and fix them there indelibly.

POTASSIUM.

Symbol K. Atomic weight 39.

Formula K_2. Probable molecular weight 78.

Memoranda.—The chief sources of the potassium salts* are the chloride found at Stassfurt, in Prussia, in the form of the mineral *Carnallite* (chloride of potassium 50, chloride of sodium 25, and chloride of magnesium 25, in 100 parts); the nitrate found in soils, especially in warm countries; and the compounds of potassium existing in plants. *Kainit*, a double sulphate of potassium and magnesium, also occurs among the Stassfurt minerals. The vegetable salts of potassium are converted into carbonate (other salts are present) when the wood or other parts are burned to ashes. If the ashes be lixiviated with water, and the solution evaporated to dryness, the residue, when fused, constitutes *crude potashes*. The residue, calcined on the hearth of a reverberatory furnace till white, gives the product termed *pearlash*. Large quantities of carbonate are thus produced in North America and Russia, and, latterly, from the sugar-beet marc, in France. From the native chloride and from the carbonate purified by treating the pearlash with its own weight of distilled water, filtering and evaporating the solution until it thickens, and stirring constantly, "so as to form a granular salt" (*Potassii Carbonas*, U. S. P.), nearly all other compounds of potassium are made. Exceptions occur in cream of tartar (*Potassii Bitartras*, U. S. P.), which is the more or less purified natural potassium salt of the grape-vine, and in nitrate of potassium. Potassium is a constituent of between forty and fifty chemical or Galenical preparations of the British Pharmacopœia.

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* The ill-defined term *salt* includes most solid chemical substances, but more especially those which assume a crystalline form.

Carbonate of potassium is a white crystalline or granular powder, insoluble in alcohol, very soluble in water, rapidly liquefying in the air through absorption of moisture, alkaline and caustic to the taste. It loses all water at a red heat. *Potassii Carbonas Purus*, U. S. P., is obtained by heating the bicarbonate to redness: the resulting white anhydrous carbonate is converted into hydrous granular carbonate by solution in water and evaporation until a dry granular salt remains.

Preparation.—Potassium itself is isolated with some difficulty by distilling a mixture of its carbonate and charcoal. It rapidly oxidizes in the air, and hence is always kept below the surface of mineral naphtha, a liquid containing no oxygen. It crystallizes in octahedra.

Quantivalence.—The atom of potassium is univalent, K'.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

These are actions utilized in manufacturing preparations of potassium. The word *synthesis* is from σύνθεσις (*sūnthēsis*), a putting together, as opposed to analysis, from ἀναλύω (*analuo*), I resolve.

Hydrate of Potassium. Caustic Potash.

First Synthetical Reaction.—Boil together, for a few minutes, in a test-tube, five or six grains of carbonate of potassium (K_2CO_3) and a like quantity of slaked lime ($Ca2HO$) with a small quantity of water. Set the mixture aside in the test-tube rack till all solid matter has subsided.

This liquid is a solution of caustic potash, or hydrate of potassium (KHO). Made of a prescribed strength (about 5 per cent.; sp. gr. 1.036), it forms the *Liquor Potassæ*, U. S. P.

The mixture is known to be boiled long enough when a little of the clear liquid, poured into another test-tube and warmed, gives no effervescence on the addition of an acid (sulphuric, hydrochloric, or acetic)—a test whose mode of action will be explained hereafter.

In the United States Pharmacopœia the carbonate of potassium for this operation is directed to be obtained by boiling a solution of the bicarbonate until effervescence ceases; that is, until the bicarbonate is almost entirely converted into carbonate.

Best Method of expressing Decompositions.—This will be easy of comprehension if what has already been stated concerning symbols and formulæ, on pages 31 to 42, has been carefully and thoughtfully considered. The best means of showing on paper the action which occurs when chemical substances attack each other is by the employment either of equations or diagrams, setting forth the formulæ of the molecules concerned in the reaction. In an *equation* the formulæ of the salts used are written on one line, the sign of addition (+) intervening; the sign of equality (=) follows, and then the formulæ of the salts produced, also separated by a plus sign (+). Thus:—

$$K_2CO_3 + Ca2HO = 2KHO + CaCO_3.$$

In this reaction (the operation just performed) the metals of the molecules of the two salts change place: from K_2CO_3 and $Ca2HO$ there are produced $CaCO_3$ and KHO (two molecules, $2KHO$): from carbonate of potassium and hydrate of calcium there result carbonate of calcium (the insoluble portion) and hydrate of potassium (in solution).*

In constructing a *diagram* or pictorial illustration of a chemical reaction (the reaction, for instance, just described), *first* the formulæ of the salts used are written under each other on the left side of the leaf of a note-book, thus:—

K_2CO_3

$Ca2HO$

Such formulæ are, in this Manual, always given with the description of the reaction. *Secondly*, on the right is then written the formula of the chief substance produced, thus:—

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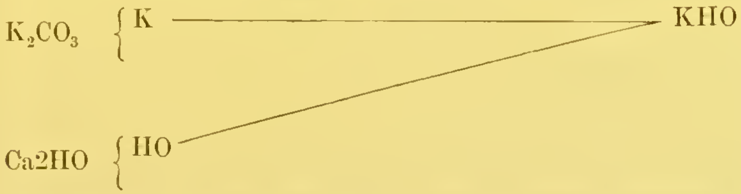
* If the student is already accustomed to the use of ordinary equations, he may pass on to *Note* 1, on page 64. If not, the author would strongly recommend the temporary employment of diagrams for expressing chemical changes. Indeed, the occasional, if not the regular, use of graphic equations or diagrams is of advantage to all students. For while equation or diagram equally well records the formulæ of the salts concerned in the whole reaction, the diagram alone suggests the *mode* in which its writer believes the respective atoms to change their positions. In the paragraphs succeeding the above, detailed explanations are given respecting the use and construction of diagrams.

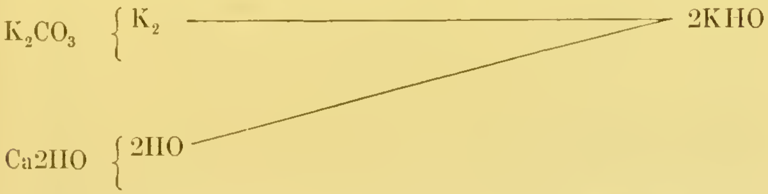
K_2CO_3 KHO

Ca2HO

Thirdly, the formation of this chief body under consideration, that is to say, both the origin of its elements and their destination, is traced out by the help of brackets which show the source of the elements, and converging lines which suggest the approach and final union of the elements, thus:—



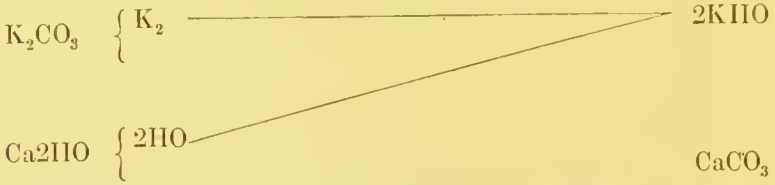
At this stage (at other stages, perhaps, in other reactions) the reader's own intelligent power of thought and reflection must come into exercise. He must reason somewhat as follows: "I am converting, and entirely converting, a quantity of carbonate of potassium into hydrate of potassium. A molecule, the smallest quantity I can picture on paper, of the carbonate of potassium (K_2CO_3) contains, I am told, two atoms of potassium (K_2), and a molecule of the hydrate (KHO), one atom (K). Therefore each molecule of the carbonate (K_2CO_3) will furnish two molecules of the hydrate (2KHO). Moreover, I notice that in the formula of a molecule of the hydrate of calcium (slaked lime) I employ, there are 2 of the HO (that is, 2HO), and this fact confirms me in the deduction that one molecule of the carbonate affords two molecules of the hydrate." The pupil will then amend his diagram, thus:—



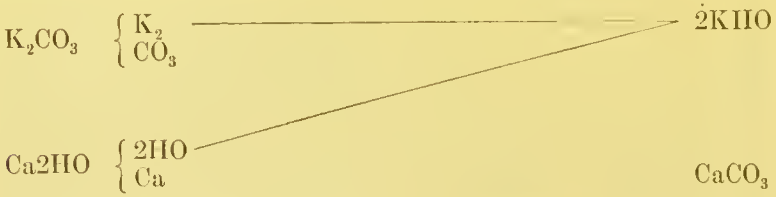
Fourthly, the question as to what becomes of the other elements must be cleared up. Indeed, when the reader remembers that he is studying this reaction for the aid it affords him in learning chemistry, and not because he is desirous of manufacturing caustic potash, he will see that this latter part of the reaction is quite as important as the former. To complete the diagram, then, he must first know what other compound is produced and its formula. The context of his Manual will generally afford this information, or, after a little experience is acquired, analogies or his own knowledge will suggest correct formulæ. In this case carbonate of calcium is produced,

$CaCO_3$. (This product is, in fact, precipitated chalk, together with any excess of slaked lime and any natural impurities in the slaked lime. *Pure* "precipitated chalk" is made by an analogous reaction described subsequently.)

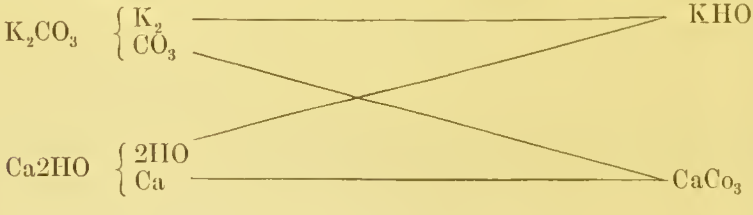
The source of the elements of the carbonate of calcium, and, finally, their union, must be indicated just as the source and mode of formation of the potash were indicated. That is to say, after the formula of this second substance produced ($CaCO_3$) is written on the right of the diagram, thus:—



the source of its elements is shown by writing the symbols for those elements on the right of the bracket attached to the formula containing the symbols of the elements, thus:—



Lines converging from the symbols of the elements and uniting at the formula of the substance are then drawn, to suggest approach of the atoms of the elements and their union to form a molecule of the compound. The diagram will now be complete, thus:—



The formation of a third product or a fourth product would be indicated in a similar manner.

Note 1.—It will be seen that the chief data required in making either equationary or diagrammatic notes of decompositions are the symbolic formulæ of the various compounds employed and produced. These formulæ are, in this Manual, given whenever necessary. Chemists obtain them in the first instance by help of quantitative analysis. By the same means is obtained a check on the probabilities respecting the relative number of molecules concerned in a reaction.

Note 2.—While an equation or a diagram is an attempt to picture the reaction which ensues when molecules of different substances act upon one another, it necessarily only represents two or a minimum number of the molecules. The student will, of course, understand that what is true of these two or three molecules is true of the thousands or millions of molecules forming the mass or whole quantity of material on which he experiments.

Note on Nomenclature.—*Hydrates* are bodies indirectly or directly derived from water by one-half of its hydrogen becoming displaced by an equivalent quantity of another radical. Thus, a piece of potassium thrown on to water (HHO) instantly liberates hydrogen, hydrate of potassium (KHO) being formed. The temperature produced at the same time is sufficiently high to cause ignition of the hydrogen, which burns with a purple flame (owing to the presence of a little vapor of potassium), while the hydrate of potassium remains dissolved in the bulk of the water. This radical or root or group of elements (HO), common to all hydrates, is sometimes termed *hydroxyl.* Water might be termed hydrate of hydrogen or hydroxylide of hydrogen.

Explanation.—With regard to the group of atoms represented by the symbols CO_3 and HO, only a few words need be said here. The former (CO_3) is the grouping (root or radical) found in all carbonates; it is termed the carbonic radical, and is as characteristic of carbonates as potassium (K) is of potassium salts. HO (hydroxyl) is characteristic of all hydrates. CO_3 is a bivalent root, HO is univalent; hence CO_3 is found united with two univalent atoms, as in carbonate of potassium, K_2CO_3, or with one bivalent atom, as in carbonate of calcium, $CaCO_3$; and HO is found united in single proportion with univalent atoms, as in hydrate of potassium, KHO, or in double proportion with bivalent atoms, as in hydrate of calcium, Ca2HO. The quantivalence of a metal has only to be learnt, and the formulæ of its carbonate and hydrate are ascertained without seeing the formula of either. The formulæ of all other metallic salts are constructed on the same principle. But, beyond committing to memory the formulæ and quantivalence of the various groupings characteristic of carbonates, hydrates, nitrates, sulphates, acetates, etc. (see the following Table), special attention should not at present be devoted to the subject of the constitution of salts, but restricted to what may be called the metallic or basylous side of salts. The formulæ and quantivalence of the chief acidulous groupings referred to and the symbols and quantivalence of allied elementary bodies are included in the following Table:—

Formulæ and Quantivalence of Acidulous Radicals.

All chlorides contain . . .	Cl	Univalent radicals.
“ bromides “ . . .	Br	
“ iodides “ . . .	I	
“ cyanides “ . . .	CN	
“ hydrates “ . . .	HO	
“ nitrates “ . . .	NO_3	
“ chlorates “ . . .	ClO_3	
“ acetates “ . . .	$C_2H_3O_2$	
“ oxides “ . . .	O	Bivalent radicals.
“ sulphides “ . . .	S	
“ sulphites “ . . .	SO_3	
“ sulphates “ . . .	SO_4	
“ carbonates “ . . .	CO_3	
“ oxalates “ . . .	C_2O_4	
“ tartrates “ . . .	$C_4H_4O_6$	
“ citrates “ . . .	$C_6H_5O_7$	Trivalent radicals.
“ phosphates “ . . .	PO_4	
“ borates “ . . .	BO_3	

Radicals.—The above elements and compounds are termed *radicals*, each being the common *root* (*radix*) in a series of salts. Why compound radicals (as NO_3, SO_4, PO_4, etc.) differ in quantivalence cannot well be explained. Their constituent atoms doubtless always exert the same amount of attractive force, nearly but not quite all this force being exerted in retaining the atoms in one group, and the remainder probably determining the quantivalence. Some of the compound radicals are obtainable in the free state, others have yet to be proved capable of isolated existence.*

Pure Solution of Potash.—Solution of potash generally contains a trace of alumina dissolved from the lime by the hot alkali, but not enough to interfere with the use of the liquid in medicine. If the solution is required for analytical purposes, it may be obtained free from alumina by avoiding the employment of heat, in the manner suggested by Redwood. Half a gallon is made by mixing half a pound of slaked lime with about three pints of water, placing the mixture in a half-gallon bottle, and adding to it, in small quantities at a time, a solution of half a pound of carbonate of potassium dissolved in the other pint of water, shaking the mixture well for several minutes after each addition. The whole is now set on one side till clear; and then, if a small quantity poured into a test-tube and warmed does not effervesce on the addition of hydrochloric acid, the solution is fit for use. If effervescence (due to carbonic acid gas) occurs, the mixture must be again well shaken. If the lime be good and recently slaked, and the bottle violently shaken once every half hour, the decomposition will be complete in about ten or twelve hours.

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* Some modern authors term these roots *radicles*, a word more usefully expressive of little roots or rootlets.

Solid Potash.—Solution of potash evaporated to dryness in a silver or clean iron vessel and the residue fused and poured into moulds constitutes *Potassa*, U. S. P. It often contains chlorides, detected by nitrate of silver; sulphates, detected by a barium salt, as described subsequently in connection with hydrochloric and sulphuric acids; and silica, which is precipitated on adding a strong solution to twice the quantity of alcohol. *Liquor Potassæ*, U. S. P., may be made by dissolving 56 parts of this hydrate in 944 of distilled water, or a corresponding quantity of potassa of any strength in water so as to make 1000 parts by weight. *Potassa cum Calce*, U. S. P., is a grayish-white powder, made by rubbing together equal weights of solid potash and quicklime.

Sulphurated Potash.

Second Synthetical Reaction.—Into a test-tube put a few grains of carbonate of potassium previously mixed with half its weight of sulphur. Heat the mixture gradually until it ceases to effervesce. The resulting fused mass poured on a slab and quickly bottled is the *Potassa Sulphurata*, Sulphurated Potassa, U. S. P.

$3K_2CO_3$	$+$	$4S_2$	$=$	$K_2S_2O_3$	$+$	$2K_2S_3$	$+$	$3CO_2$
Carbonate of potassium.		Sulphur.		Hyposulphite of potassium.		Sulphide of potassium.		Carbonic acid gas.

As met with in pharmacy this salt is not a single definite chemical compound, but a mixture of several; in short, its chemical character is well indicated by its vague name. When fresh, and if carefully prepared with the official proportions of dry ingredients, it is of the color of liver (whence the old name "liver of sulphur"), and consists, as shown by J. Watts, of the salts mentioned in the foregoing equation, together with a little undecomposed carbonate of potassium, with perhaps higher sulphides of potassium (K_2S_4 and K_2S_5); but, rapidly absorbing oxygen from the air, it soon becomes green and yellow, sulphite (K_2SO_3) and sulphate of potassium (K_2SO_4) are formed, and ultimately a useless mass of dirty-white color results, consisting of sulphate and hyposulphite, with generally some carbonate of potassium and free sulphur. Moreover, if overheated in manufacture, the hyposulphite $4(K_2S_2O_3)$ is decomposed into sulphate $3(K_2SO_4)$ and sulphide (K_2S_5) of potassium. Recently made, "about three-fourths of its weight are dissolved by rectified spirit." It is occasionally employed in the form of ointment.

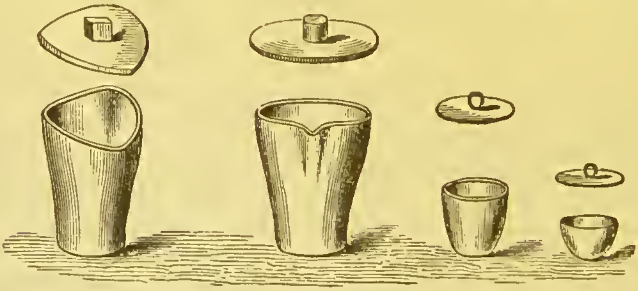
"On triturating together 10 parts of Sulphurated Potassa and 12.69 parts of crystallized sulphate of copper with 60 parts of water, and filtering, the filtrate should remain unaffected by hydrosulphuric acid (presence of at least 56 per cent. of true sulphide of potassium)." U. S. P.

The extremely, indeed most unusually, complicated nature of the reaction, will probably cause failure to any attempt by a student to draw out an equation or a diagram of the reaction without the aid of the printed equation given above. He may therefore content himself, in this case, by introducing into his note-book a diagram founded directly on the equation and on the numbers of molecules there stated. With this printed equation, and the details of construction of diagrams given in connection with the first synthetical reaction, he will be able to give a diagram of this second synthetical reaction without troubling his reasoning powers, while at the same time he will be familiarizing himself with the more mechanical portions of a diagram.

In preparing large quantities of sulphurated potash, the test-tube is replaced by an earthenware vessel termed a *crucible* (from *crux*, a cross, for originally a cross was impressed upon the melting-pot as used by alchemists and goldsmiths; others derive the word from crux, an instrument of torture, the sense here being symbolical).

Heating Crucibles.—Crucibles of a few ounces' capacity may be heated in an ordinary grate-fire. Larger ones require a stove with a good draught—that is, a *furnace.* Even the smaller ones are more conveniently and quickly heated in a furnace. Half-ounce or one-ounce experimental porcelain crucibles may be heated in a spirit- or gas-flame; the air-gas flame already described being generally the most suitable.

Fig. 12. Fig. 13. Fig. 14.



Crucibles of various forms.

Acetate of Potassium.

Third Synthetical Reaction.—Place ten or twenty or more grains of carbonate of potassium in a small dish, and *saturate* (*satur*, full) with acetic acid; that is, add acetic acid so long as effervescence is thereby produced; the resulting liquid is a strong solution of acetate of potassium.

Evaporate most of the water in an open dish (see Figs. 15, 16), stirring with a glass rod* to promote the evolution of vapor; a white salt remains, which fuses on the further application of heat. This is the official Acetate of Potassium (*Potassii Acetas*, U. S. P.). If fused in the open vessel the acetate is liable to become slightly charred and discolored; this is prevented by transferring the solid residue to a test-tube or Florence flask before finally fusing. It forms a white, deliquescent, foliaceous, satin-like mass, neutral to test-paper, and wholly soluble in spirit. A ten per cent. solution in water forms the "Solution of Acetate of Potash," B. P.

$$\underset{\substack{\text{Carbonate of}\\\text{potassium.}}}{K_2CO_3} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{2HC_2H_3O_2} = \underset{\substack{\text{Acetate of}\\\text{potassium.}}}{2KC_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

Explanation of Formulæ.—The formula for one molecule of acetic acid (the acetate of hydrogen) is $HC_2H_3O_2$, and one of acetate of potassium, $KC_2H_3O_2$. The grouping, $C_2H_3O_2$, is characteristic of all acetates; it is univalent, and may be shortly though less instructively written $\bar{A}$.

Explanation of Process.—When two molecules of acetic acid ($2HC_2H_3O_2$) and one of carbonate of potassium (K_2CO_3) react, two molecules of acetate of potassium ($2KC_2H_3O_2$) and one of carbonic acid (H_2CO_3) are produced, the latter at once splitting up into water (H_2O) and carbonic acid gas (CO_2), as already shown in the equation.

Diagram of the Reaction.—The nature of the above operation is indicated by an *equation;* it (and succeeding reactions) should be expressed in the student's note-book as a *diagram*, and, if possible, without the aid of the equation.

Note.—The above reaction has a general as well as a special synthetical interest. It represents one of the commonest methods of forming salts, namely, the saturation of an acid with a carbonate. Carbonates added to acetic acid yield acetates, to nitric acid nitrates, to sulphuric acid sulphates. Many illustrations of this general process occur in pharmacy.

Evaporation of water from a liquid is best conducted in wide shallow vessels rather than in narrow deep ones, as the steam can thus quickly diffuse into the air and be rapidly conveyed away; hence a small round-bottomed basin, heated as shown in Fig. 15, is far more suitable than a test-tube for such operations. On the manufacturing scale, iron, or iron lined with enamel or semi-porcelain, copper, tinned copper, or solid tin pans are used. Up to 12 or 18 inches diameter, pans, basins, or dishes, made of Wedgwood ware or porcelain composition (Fig. 16), may be employed. Small dishes may be

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* Glass rod is usually purchased in the form of long sticks. The pieces may be cut to convenient lengths of from 6 to 12 inches (*vide* p. 17), sharp ends being rounded off by holding in a flame for a few minutes.

Fig. 15.

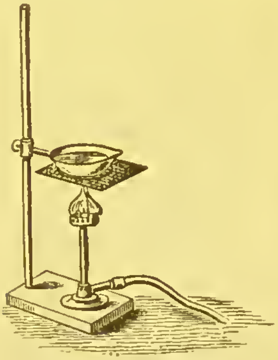
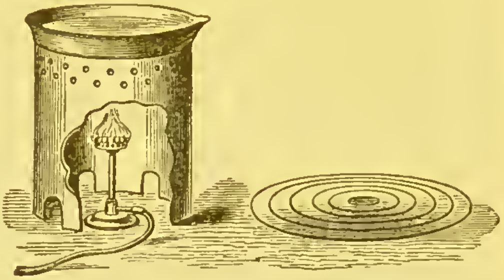


Fig. 16.



Evaporation from small and large basins.

supported by retort-stands (Fig. 15), larger by cylinders (Fig. 16), to which the dish is, if less in diameter than the cylinder, adapted by such flat rings or diaphragms as are shown in the figure.

Bicarbonate of Potassium.

Fourth Synthetical Reaction.—Make a *strong* solution of carbonate of potassium by heating in a test-tube a mixture of several grains of the salt with rather less than an equal weight of water. Through the cooled solution pass carbonic acid gas slowly but continuously; after a time a white crystalline precipitate of Acid Carbonate or Bicarbonate of Potassium ($KHCO_3$), *Potassii Bicarbonas*, U. S. P., the Bicarbonate of Potash of old Pharmaçopœias, will be formed.

$$\underset{\substack{\text{Carbonate of}\\\text{potassium.}}}{K_2CO_3} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2} = \underset{\substack{\text{Bicarbonate}\\\text{of potassium.}}}{2KHCO_3}$$

The carbonic acid gas necessary for this operation is to be prepared from marble, though it might be obtained from any carbonate. Thus the previous synthetical reaction could be made available for this purpose, the carbonic acid gas evolved on the addition of the acetic acid to the carbonate of potassium being conducted into a strong solution of more carbonate of potassium by a glass tube bent and fitted as described when treating of oxygen gas. But motives of economy induce the use of carbonate of calcium, the form known as marble being always employed. Economy and convenience also cause hydrochloric acid to be used in preference to acetic or any other.

Generate the carbonic acid gas by adding common hydrochloric acid, diluted with twice its bulk of water, to a few fragments of marble contained in a test-tube or small flask, and conduct the gas into the solution of carbonate of potassium by a glass tube bent to a convenient angle or angles, and fitted to the test-tube by a cork in the usual way. (See Fig. 10, though no heat is necessary.) The tube may be replenished with marble, or acid, or both, when the evolution of gas is becoming slow. In working on any larger quantity than a few grains of the carbonate, a wide delivery-tube should be employed, or the end of the narrow tube occasionally cleared from any bicarbonate that may have been deposited in it. The more economical official arrangements of the apparatus employed in this process will be described under the corresponding sodium salt.

Deposition of the Bicarbonate explained.—Bicarbonate of potassium is to a certain extent soluble in water; but as it is less so than the carbonate of potassium, and as a *saturated* solution of the latter has been used, the precipitation of a part of the bicarbonate inevitably occurs. In other words, the quantity of water present is sufficient to keep the carbonate, but insufficient to retain the equivalent quantity of bicarbonate, in solution.

Properties.—Prepared on the large scale, bicarbonate of potassium occurs in colorless, non-deliquescent, right rhombic prisms; it has a saline, feebly alkaline, non-corrosive taste. Heated to redness, it loses 31 per cent of its weight, and is converted into carbonate (K_2CO_3), water (H_2O), and carbonic acid gas (CO_2).

$$\underbrace{2KHCO_3}_{\substack{2)\underline{200} \\ 100}} = \underbrace{K_2CO_3}_{\substack{2)\underline{138} \\ 69}} + \underbrace{\underbrace{H_2O}_{\substack{2)\underline{18} \\ 9}} + \underbrace{CO_2}_{\substack{2)\underline{44} \\ 22}}}_{31}$$

The foregoing equation and accompanying molecular weights (see page 54) show how bicarbonate of potassium, the molecular weight of which happens to be just 100, *must* lose 31 per cent. when completely decomposed by heat. By ebullition of its solution it also is soon almost wholly changed to carbonate.

Effervescing Solution of Potash.—A solution of 30 grains of bicarbonate of potassium in one pint of water, charged with 7 times its bulk (often less of carbonic) acid gas by pressure, constitutes the ordinary "potash-water," the so-called *Liquor Potassæ Effervescens*, B. P.

Notes on Nomenclature.—The prefix *bi-* in the name "bicarbonate of potassium" serves to recall the fact that to a given amount of potassium this salt contains *twice* as much carbonic radical as the carbonate. The salt is really a "carbonate of potassium and hydrogen" ($KHCO_3$); it is intermediate between carbonate of potassium

(K_2CO_3) and carbonate of hydrogen, or true carbonic acid (H_2CO_3); it is "acid carbonate of potassium" or "hydric potassium carbonate." Hence in constitution it is an acid salt, although not acid to the taste.

Salts whose specific names end in the syllable "*ate*" (carbon*ate*, sulph*ate*, etc.) are in general conventionally so termed when they contain an acidulous radical, or the characteristic elements of an acid whose name ends in "*ic*," and from which acid they have been or may be formed. Thus the syllable "*ate*," in the words sulph*ate*, nitr*ate*, acet*ate*, carbon*ate*, etc., indicates that the respective salts contain a radical whose name ended in *ic*, the previous syllables, sulph-, nitr-, acet-, carbon-, indicating what that radical was—the sulphuric, nitric, acetic, or carbonic. Occasionally a letter or syllable is dropped from or added to a word to render the name more euphonious; thus the sulphuric radical forms sulphates, not sulphurates.

Citrate of Potassium.

Fifth Synthetical Reaction.—Dissolve a few grains or more of bicarbonate (or 8 parts) of potassium in water, and add (6 parts of) citric acid ($H_3C_6H_5O_7$) until it no longer causes effervescence. The resulting liquid is a solution of citrate of potassium ($K_3C_6H_5O_7$) (*Liquor Potassii Citratis*, U. S. P., sp. gr. 1.059). Evaporated to dryness, in an open dish, a pulverulent or granular residue is obtained, which is the official *Potassii Citras*, U. S. P., a white deliquescent powder.

$$\underset{\text{Carbonate of potassium.}}{3KHCO_3} + \underset{\text{Citric acid.}}{H_3C_6H_5O_7} = \underset{\text{Citrate of potassium.}}{K_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

Citrates.—The citric radical or group of elements, which with three atoms of hydrogen forms a molecule of citric acid, and with three of potassium citrate of potassium, is a trivalent grouping; hence the three atoms of potassium in a molecule of the citrate. The full chemistry of citric acid and other citrates will be subsequently described.

Nitrate of potassium (KNO_3) (*Potassii Nitras*, U. S. P.) and *Sulphate of potassium* (K_2SO_4) (*Potassii Sulphas*, U. S. P.) could obviously also be made by saturating nitric acid (HNO_3), and sulphuric acid (H_2SO_4), respectively, by carbonate of potassium. Practically, they are not made in that way—the nitrate occurring, as already stated, in nature, and the sulphate as a by-product in many operations. Both salts will be hereafter alluded to in connection with nitric acid.

Tartrate of Potassium.

Sixth Synthetical Reaction.—Place a few grains of carbonate of potassium in a test-tube with a little water, heat to the boiling-point, and then add acid tartrate of potassium ($KHC_4H_4O_6$ or $KH\overline{T}$) till there is no more effervescence; a solution of neutral tartrate of potassium (K_2T) results, the *Potassii Tartras* of the United States Pharmacopœia, the old "Soluble Tartar." Crystals (4- or 6-sided prisms) may be obtained on concentrating the solution by evaporation and setting the hot liquid aside. Larger quantities are made in the same way, 20 of acid tartrate and 9 of carbonate (with 50 of water) being about the proportions necessary for neutrality.

$$\underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Carbonate of potassium.}}{K_2CO_3} = \underset{\text{Neutral tartrate of potassium.}}{2K_2C_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Tartrates.—$C_4H_4O_6$ are the elements characteristic of all tartrates; they form a bivalent grouping; hence the formula of the hydrogen tartrate, or tartaric acid, is $H_2C_4H_4O_6$; that of the potassium tartrate $K_2C_4H_4O_6$; of the intermediate salt, the acid potassium tartrate (cream of tartar), $KHC_4H_4O_6$. If the acid tartrate of one metal and the carbonate of another react, a neutral dimetallic tartrate results, as seen in Rochelle salt ($KNaC_4H_4O_6, 4H_2O$), the *Soda Tartarata* of the British Pharmacopœia (*Potassii et Sodii Tartras*, U. S. P.).

Acid salts (*e. g.* $KHC_4H_4O_6$), that is, salts intermediate in composition between a normal or neutral salt (*e. g.* $K_2C_4H_4O_6$) and an acid (*e. g.* $H_2C_4H_4O_6$), will frequently be met with. All acidulous radicals, except those which are univalent, may be concerned in the formation of such acid salts.

Iodide of Potassium.

Seventh Synthetical Reaction.—To a solution of potash, heated in a test-tube, or flask, or an evaporating-basin, according to quantity, add a small quantity of solid iodine. The deep color of the iodine disappears entirely. This is due to the formation of the colorless salts, iodide of potassium (KI) and iodate of potassium (KIO_3), which remain dissolved in the liquid. Continue the addition of iodine so long as its color, after a few minutes' warming and stirring, disappears. When the whole of the potash in the solution of potash has been converted into the salts mentioned, the slight excess of iodine remaining in the liquid will color it, and thus show that this stage of the operation is completed.

$$\underset{\text{Hydrate of potassium.}}{6KHO} + \underset{\text{Iodine.}}{3I_2} = \underset{\text{Iodide of potassium.}}{5KI} + \underset{\text{Iodate of potassium.}}{KIO_3} + \underset{\text{Water.}}{3H_2O}$$

Separation of the Iodide from the Iodate.—Evaporate the solution to dryness. If each salt were required, the resulting solid mixture might be digested in spirit of wine, which dissolves the iodide, but not the iodate. But the iodide only is used in medicine. Mix the residue, therefore (reserving a grain or two for a subsequent experiment), with about a twelfth of its weight of charcoal, and gently heat in a test-tube or crucible until slight deflagration ensues.*

The crucible may be held in a spirit or air-gas flame, or other fire, by tongs. (Scissors-shaped and other "crucible-tongs" are sold by all makers of apparatus.) Under these circumstances the iodide remains unaffected; but the iodate loses all its oxygen, and is thus also reduced to the state of iodide.

$$\underset{\substack{\text{Iodate of}\\\text{potassium.}}}{2KIO_3} + \underset{\text{Carbon.}}{3C_2} = \underset{\substack{\text{Iodide of}\\\text{potassium.}}}{2KI} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{6CO}$$

Treat the mass with a little water, and filter to separate excess of charcoal; a solution of pure iodide of potassium results. (*Potassii Iodidum*, U. S. P.) The latter may be used as a reagent or it may be evaporated to a small bulk and set aside to crystallize.

"Solution of Iodate of Potassium" is official (B. P.) as a test-liquid.

Properties.—Iodide of potassium crystallizes in small cubical crystals, very soluble in water, less so in spirit. One part in twenty of water forms "Solution of Iodide of Potassium," U. S. P. Exposed to air and sunlight, pure iodide of potassium becomes slightly brown owing to the liberation of iodine. Under these circumstances a little carbonate of potassium is produced by action of the atmospheric carbonic acid and a little hydriodic acid (HI) is set free, and the latter, attacked by oxygen, yields a trace of water and of free iodine. The ozone in the air (see "Ozone" in Index) may also contribute to the liberation of iodine from such compounds as iodide of potassium.

The addition of charcoal in the above process is simply to facilitate the removal of the oxygen of the iodate of potassium. Iodate of potassium (KIO_3) is analogous in constitution, and in composition, so far as the atoms of oxygen are concerned, to chlorate of potassium ($KClO_3$), which has already been stated to be more useful than any other salt for the actual preparation of oxygen gas itself. Hence the removal of the oxygen of the iodate might be accomplished by heating the residue without charcoal. In that case the liberated oxygen would be detected on inserting the incandescent extremity of a strip of wood into the mouth of the test-tube in which the mixture of iodide and iodate had been heated. The charcoal, however, burns out the oxygen more quickly, and thus economizes both heat and time.

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* If, in the operation of heating iodate of potassium with charcoal, excess of the latter be employed, slight incandescence rather than deflagration occurs; if the charcoal be largely in excess, the reduction of the iodate to iodide of potassium is effected without visible deflagration or even incandescence.

Deflagration means violent burning, from *flagratus*, burnt (*flagro*, I burn), and *de*, a prefix augmenting the sense of the word to which it may be attached. Paper thrown into a fire simply burns, nitre deflagrates. *De*-tonate (*detono*) is a precisely similar word, meaning to explode with violent noise.

Note.—The formula of iodide of potassium (KI) shows that the salt contains potassium and iodine in atomic proportions. A reference to the table of atomic weights at the end of the volume, and a rule-of-three sum, would therefore show what weight of salt is producible from any given weight of iodine.

Detection of Iodate in Iodide of Potassium.—Iodate of potassium remaining as an impurity in iodide of potassium may be detected by adding to a solution of the latter salt some weak acid (say tartaric), shaking, and then adding mucilage of starch; blue "iodide of starch" is formed if a trace of iodate be present, not otherwise. By the reaction of the added acid and the iodate of potassium, iodic acid (HIO_3) is produced, and by reaction of the added acid and the iodide of potassium, hydriodic acid (HI) is produced; neither of these two acids alone attacks starch, but by reaction on each other they give rise to free iodine, which then forms the blue color. This experiment should be tried on a sample of pure iodide of potassium and on a grain or two of the impure iodide reserved from the previous experiment.

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

Note on Nomenclature.—The syllable *ide* attached to the syllable *iod*, in the name "iodide of potassium," indicates that the element *iodine* is combined with the potassium. An iod*ate*, as already explained, is a salt containing the characteristic elements of iod*ic* acid and of all iodic compounds. Salts one of whose names ends in *ide* are those which are, or may be, formed from elements. The names of salts which are, or may be, formed from compounds include other syllables, *ate* being one (see page 72). The only other syllable is *ite*, which is included in the names of salts which are, or may be, formed from acids and radicals whose names end in *ous*: thus hyposulph*ite* of sodium, etc. To recapitulate: A salt, whose name ends in *ate* contains a compound acidulous radical whose name ends in *ic*; a salt whose name ends in *ite* contains a compound acidulous radical whose name ends in *ous*; a salt whose name ends in *ide* contains an element for its acidulous radical. Thus sulph*ide* relates to sulphur, sulph*ite* to the sulphurous radical, sulph*ate* to the sulphuric radical, and so on with other "ides," "ites," or "ates."

Bromide of Potassium (*Potassii Bromidum*, U. S. P.)—This salt is identical in constitution with iodide of potassium, and may be made in exactly the same way, bromine being substituted for iodine. The formula of bromic acid is $HBrO_3$. It will be noticed that the following equations are similar in character to those showing the preparation of iodide of potassium:—

$$\underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{6KHO} + \underset{\text{Bromine.}}{3Br_2} = \underset{\substack{\text{Bromide of}\\\text{potassium.}}}{5KBr} + \underset{\substack{\text{Bromate of}\\\text{potassium.}}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\substack{\text{Bromate of}\\\text{potassium.}}}{2KBrO_3} + \underset{\text{Carbon.}}{3C_2} = \underset{\substack{\text{Bromide of}\\\text{potassium.}}}{2KBr} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{6CO}$$

Bromide of potassium may also be made by decomposing solution of bromide of iron ($FeBr_2$) by solution of pure carbonate of potassium (K_2CO_3), evaporating and crystallizing.

Manganates of Potassium.

Eighth Synthetical Reaction.—Place a fragment of solid caustic potash (KHO), with about the same quantity of chlorate of potassium ($KClO_3$), and of black oxide of manganese (MnO_2) on a piece of platinum foil.* Hold the foil by a small pair of forceps or tongs in the flame of a blowpipe for a few minutes until the fused mixture has become dark green—apparently black. This color is that of *manganate of potassium* (K_2MnO_4).

$$\underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{6KHO} + \underset{\substack{\text{Chlorate of}\\\text{potassium.}}}{KClO_3} + \underset{\substack{\text{Black oxide of}\\\text{manganese.}}}{3MnO_2} = \underset{\substack{\text{Manganate of}\\\text{potassium.}}}{3K_2MnO_4} + \underset{\substack{\text{Chloride of}\\\text{potassium.}}}{KCl} + \underset{\text{Water.}}{3H_2O}$$

Ninth Synthetical Reaction.—*Permanganate of Potassium* ($K_2Mn_2O_8$) (*Potassii Permanganas*, U. S. P.), which is purple, is obtained, or rather a solution of it, on placing the foil and its adherent mass in water, and boiling for a short time.

$$\underset{\substack{\text{Manganate of}\\\text{potassium.}}}{3K_2MnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Permanganate}\\\text{of potassium.}}}{K_2Mn_2O_8} + \underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{4KHO} + \underset{\substack{\text{Black oxide}\\\text{of manganese.}}}{MnO_2}$$

On the large scale, the potash set free in the reaction is neutralized by sulphuric or carbonic acid, and the solution evaporated to the crystallizing point. Further details will be given in connection with manganese.

Solutions of manganate or permanganate of potassium and of sodium so readily yield their oxygen to organic matter, that they are used on the large scale as disinfectants, under the name of "Condy's Disinfecting Fluids."

Synthetical Reactions bringing under consideration the remaining official compounds (namely, bichromate, arsenite, chlorate, cyanide, ferrocyanide, and ferridcyanide of potassium) are deferred at present.

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* The foil may be 1 inch broad by 2 inches long. No ordinary flame will melt the platinum; fused caustic alkalies only slowly corrode it, and very few other chemical substances affect it at all; hence the same piece may be used in experimenting over and over again. Most metals form a fusible alloy with platinum, and phosphorus rapidly attacks it, hence such substances, as well as mixtures likely to yield them, should be heated in a small porcelain crucible.

(*b*) *Reactions having Analytical Interest* (*Tests*).

Note.—These are reactions utilized in searching for small quantities of a substance (in the present instance of potassium) in a solution. They are best performed in test-tubes or other small vessels. Each should be expressed, in the form of an equation or diagram, in the student's note-book. *All previous or future equations given in this volume should be transferred to the note-book in the form of diagrams, constructed as described on pages* 63 *and* 64, *unless the student can with ease construct the equations without the aid of the manual.*

First Analytical Reaction.[*]—To a solution of any salt of potassium (chloride,[†] for example) add a few drops of hydrochloric acid and of a solution of perchloride of platinum ($PtCl_4$), and stir the mixture with a glass rod; a yellow granular or slightly crystalline precipitate[‡] slowly forms. (The precipitate is the double chloride of platinum and potassium, and its composition is expressed by the formula $PtCl_4 2KCl$.)

Memoranda.[§]—When the precipitate is long in forming, it is sometimes of an orange-yellow tint. If iodide of potassium happen to be the potassium salt under examination, some iodide of platinum (PtI_4) will also be formed, giving a red color to the solution, and a larger quantity of the *precipitant* (that is, the precipitating agent) will be required.

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[*] As already indicated, chemical reactions are scarcely analytical or synthetical in themselves, but, rather, performed with an analytical or synthetical object. Indeed, not unfrequently one and the same reaction is both a synthetical and an analytical reaction. Thus this first, so-called, "analytical reaction" is a synthetical reaction if performed with the object of preparing a specimen of the double chloride of platinum and potassium. It is an analytical reaction, or, rather, has analytical interest, if performed with the object of demonstrating the presence of potassium. Chemical reactions in themselves are operations, not so much of analysis (resolution) or synthesis (combination) or of analysis and synthesis conjoined, as of what has sometimes times been termed *metathesis* (transposition). Molecules are not torn to atoms in an operation performed with an analytical object, nor are the atoms put together or set together in an operation (perhaps the same operation) performed with a synthetical object: but in both operations the atoms of the molecules undergo metathesis, that is, exchange places, or are transposed. In short, chemists use the words "analytical" and "synthetical" in a conventional rather than a strictly etymological sense.

[†] A few fragments of carbonate of potassium, two or three drops of hydrochloric acid, and a small quantity of water, give a solution of chloride of potassium at once, $K_2CO_3 + 2HCl = 2KCl + H_2O + CO_2$.

[‡] By *precipitation* (from *præcipito*, to throw down suddenly) is simply meant the formation of particles of solid in a liquid, no matter whether the solid, the *precipitate*, subsides or floats.

[§] Experiments with such expensive reagents as perchloride of platinum are economically performed with watch-glasses, drops of the liquid being operated on.

Precaution.—Only chloride of potassium forms this characteristic compound; hence, if the potassium salt in the solution is known not to be a chloride, or if its composition is unknown, a few drops of hydrochloric acid must be added, otherwise some of the perchloride of platinum will be utilized for its chlorine only, the platinum being wasted. Thus, if nitrate of potassium (KNO_3) be present, a few drops of hydrochloric acid enable the potassium to assume the form of chloride when the perchloride of platinum is added, nitric acid (HNO_3) being set free.

Explanation.—The precipitate is, practically, insoluble in water. It is for this reason that a very small quantity of any soluble potassium salt (or, rather, of the potassium in that salt) is thrown out of solution by perchloride of platinum.

Note on Nomenclature.—When distinct molecules of salts unite and form a single crystalline compound, the product is termed a *double* salt. The double chloride of potassium and platinum is such a body.

Acid Tartrate of Potassium.

Second Analytical Reaction.—To any solution of any salt of potassium add excess of strong solution of tartaric acid ($H_2C_4H_4O_6$), and shake or well stir the mixture; a white granular precipitate of acid tartrate of potassium ($KHC_4H_4O_6$) will be formed.

Note.—By "excess" of any test liquid (such as the "solution of tartaric acid" just mentioned) is meant such a quantity as is *probably* rather more than sufficient to convert the whole weight of the compound attacked into the compound produced. Thus, in the present case enough acid must be added to convert the whole of the potassium salt operated on into acid tartrate of potassium. What the weight of salt operated on was must be mentally estimated, roughly, by the operator. It is not necessary in analyzing to know the exact weights of salts employed. The analyst must use his judgment, founded on his knowledge of the reaction (as shown by an equation) and of the molecular weights of the substances employed in the reaction as well as by the rough estimate of the amount of material on which he is experimenting.

Limits of the Test.—Acid tartrate of potassium is soluble in about 180 parts of cold and in 6 parts of boiling water. Hence, in applying the tartaric test for potassium, the solutions must not be hot. Even if cold, no precipitate will be obtained if the solutions are very dilute. This test, therefore, is of far less value than the first mentioned. The acid tartrate of potassium is less soluble in diluted alcohol than in water; so that the addition of spirit of wine renders the reaction somewhat more delicate.

Cream of Tartar.—The precipitate is the *Bitartrate or Acid Tartrate of Potassium* (*Potassii Bitartras*, U. S. P.), though the official preparation is not formed in the above manner; on the contrary, the acid is derived from the salt, which, mixed with tartrate of calcium, occurs naturally in the juice of many plants.

Memorandum.—When the tartaric acid is added to the salt of potassium, and the acid tartrate formed, the acid whose chief elements were previously with the potassium is set free; and in such acid solutions the acid tartrate is somewhat soluble. To prevent loss on this account, acid tartrate of sodium, or Bitartrate of Sodium, U. S. P., $NaHC_4H_4O_6, H_2O$, a salt tolerably soluble in water, may be used as a test instead of tartaric acid (Plunkett). The sodium, uniting with the acidulous radical, thus gives a neutral instead of an acid solution. But this advantage is of less importance from the fact that more water is introduced by the saturated solution of acid tartrate of sodium than by a saturated solution of tartaric acid.

Third Analytical Reaction.—The *flame-test.* Dip the looped end of a platinum wire into a solution containing a potassium salt, and introduce the loop into the lower part of a spirit-flame, the flame of a mixture of gas and air, a blowpipe flame, or other slightly colored flame. A light violet or lavender tint will be communicated to the flame, an effect highly characteristic of salts of potassium.

Fourth Analytical Fact.—Salts of potassium are not volatile. Place a fragment of carbonate, nitrate, or any other potassium salt, on a piece of platinum foil, and heat the latter in the flame of a lamp; the salt may fuse to a transparent liquid and flow freely over the foil, water also if present will escape as steam, and black carbon be set free if the salt happen to be a tartrate, citrate, etc.; but the potassium compound itself will not be vaporized. This is a valuable negative property, as will be evident when the analytical reactions of ammonium come under notice.

QUESTIONS AND EXERCISES.

70. Name the sources of Potassium.

71. Give the source, formula, and characters of Carbonate of Potassium.

72. Distinguish between synthetical and analytical reactions.

73. How is the official *Liquor Potassæ* prepared?

74. What is the systematic name of Caustic Potash?

75. State the chemical formula of Caustic Potash.

76. Construct an equation or diagram expressive of the reaction between Carbonate of Potassium and slaked lime.

77. Define a *hydrate.*

78. What group of atoms is characteristic of all carbonates?

79. Define the term *radical.*

80. How is "Sulphurated Potash" made, and of what salts is it a mixture?

81. What is the formula of the acetic radical—the radical of all acetates?

82. Draw a diagram showing the formation of Acetate of Potassium.

83. Give a general process for the conversion of carbonates into other salts.

84. What is the difference between Carbonate and Bicarbonate of Potassium? How is the latter prepared?

85. What is the relation between salts whose specific names end in the syllable "*ate*," and acids ending in "*ic*"?

86. Draw out diagrams or equations descriptive of the formation of Tartrate of Potassium from the Acid Tartrate, and Citrate from the Carbonate of Potassium.

87. Distinguish between a normal and an acid salt.

88. How is Iodide of Potassium made? Illustrate the process either by diagrams or equations.

89. Describe the appearance and chemical properties of Iodide of Potassium.

90. Work out a sum showing how much Iodide of Potassium is producible from 1000 grains of Iodine? Ans. 1307 grains.

91. Give a method for the detection of Iodate in Iodide of Potassium. Explain the reaction.

92. Has the syllable "*ide*" any general significance in chemical nomenclature?

93. What are the differences between sulphides, sulphites, and sulphates?

94. Mention the chemical relations of Bromide to Iodide of Potassium.

95. Describe the formation of Permanganate of Potassium, giving equations or diagrams.

96. How do manganate and permanganate of potassium act as disinfectants?

97. Enumerate the tests for potassium, explaining by diagrams or equations the various reactions which occur.

SODIUM.

Symbol Na. Atomic weight 23.

Formula Na_2. Probable molecular weight 46.

Memoranda.—Most of the sodium salts met with in Pharmacy are obtained directly from carbonate of sodium, which is now manufactured on an enormous scale from chloride of sodium (common salt, sea-salt, bay-salt, or rock-salt), the natural source of the sodium salts. When pure, salt (*Sodii Chloridum*, U. S. P.) occurs "in small white crystalline grains, or transparent cubic crystals, free from moisture;" the best varieties commonly contain a little chloride of magnesium and sometimes other impurities. Besides the direct and indirect use of carbonate of sodium, or carbonate of soda, as it is commonly called in medicine, it is largely used for household cleansing purposes under the name of "soda," and in the manufacture of soap. Nitrate of sodium also occurs in nature, but is valuable for it nitric constituents rather than its sodium. Sodium is a constituent of about forty chemical or Galenical preparations of the Pharmacopœias.

Sodium is prepared by a process similar to that for potassium, but with less difficulty. It crystallizes in octahedra. Its atom is univalent, Na′.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Reactions having Synthetical Interest.*

Hydrate of Sodium. Caustic Soda.

First Synthetical Reaction.—The formation of solution of hydrate of sodium or caustic soda, NaHO (*Liquor Sodæ*, U. S. P.). This operation resembles that of making solution of potash already described, and its strength is the same, "about 5 per cent;" sp. gr. about 1.059.

The practical student should refer to the remarks made concerning solution of potash, applying them to solution of soda. He may perform the corresponding experiments or omit them, as he considers he does or does not clearly comprehend all they are designed to teach.

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Hydrate of sodium.}}{2NaHO} + \underset{\text{Carbonate of calcium.}}{CaCO_3}$$

Pure Solution of Soda, free from any trace of alumina, may be prepared by shaking in a Winchester quart, once every 20 or 30 minutes for 5 or 6 hours, 14 ozs. of crystals of carbonate of sodium and 8 ozs. of good recently slaked lime. If solution of soda be evaporated to dryness, and the residue fused and poured into moulds, solid hydrate of sodium (*Soda*, U. S. P.) is obtained. Common and cheap caustic soda is now largely employed in various manufactures. This variety is a by-product in the preparation of carbonate of sodium, but, though highly useful as a chemical agent, is too impure for use in medicine. The United States Pharmacopœia recognizes Liquor Sodæ made from solid caustic soda 56 parts, and distilled water 944 parts; or from caustic soda of any other strength if only an equivalent amount be used.

Action of Sodium on Water.—Sodium, like potassium, decomposes water with production of hydrate of sodium and hydrogen, but unless the sodium is confined to one spot by placing it on a small floating piece of filter paper, the action is not sufficiently intense to cause ignition of the escaping hydrogen. When the latter does ignite, it burns with a yellow flame, due to the presence of a little vapor of sodium.

Second Synthetical Reaction.—The reaction of sulphur and carbonate of sodium at a high temperature resembles that of sulphur and carbonate of potassium; but, as the product is not used in medicine, the experiment may be omitted. It is mentioned here to draw attention to the close resemblance of the potassium salts to those of sodium.

Acetate of Sodium.

Third Synthetical Reaction.—Add the powder or fragments of carbonate of sodium (Na_2CO_3) to some strong acetic acid in a test-tube or evaporating-basin as long as effervescence occurs, and then evaporate some of the water.* When the solution is cold, crystals of acetate of sodium ($NaC_2H_3O_2,3H_2O$) (*Sodii Acetas*, U. S. P.) will be deposited. A ten per cent. solution in distilled water forms the "Solution of Acetate of Soda," B. P.

Acetate of sodium effloresces in dry air, and loses all its water of crystallization when gently heated. It supports a temperature of 270° or 280° F. without decomposition, but above 300° soon chars.

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of sodium.}}{2NaC_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Bicarbonate of Sodium.

Fourth Synthetical Reaction.—The action of carbonic acid (H_2CO_3) or carbonic acid gas (CO_2) and water (H_2O), on carbonate of sodium (Na_2CO_3). This resembles that of carbonic acid on carbonate of potassium, but is applied in a different manner. The result is bicarbonate of sodium ($NaHCO_3$) (*Sodii Bicarbonas Venalis*, U. S. P.).

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2} = \underset{\text{Bicarbonate of sodium.}}{2NaHCO_3}$$

Process.—Heat crystals of carbonate of sodium in a porcelain crucible until no more steam escapes. Rub the product, in a mortar, with two-thirds its weight of more of the crystals and place the powder in a test-tube or small bottle into which carbonic acid gas may be conveyed by a tube passing through a cork and terminating at the bottom of the vessel. To generate the carbonic acid gas fill a test-tube having a small hole in the bottom (or a similar piece of glass tubing, of which one end is plugged by a grooved cork) with fragments of marble, insert a cork and delivery-tube, and connect the latter with the similar tube of the vessel containing the carbonate of sodium by a piece of India-rubber tubing. Now plunge the tube of marble into a test-glass, or other vessel, containing a mixture of one part hydrochloric acid and two parts water, and loosen the cork of the carbonate-of-sodium tube until carbonic acid gas, generated in the marble tube, may be considered to fill the whole arrangement; then replace the cork tightly and set the apparatus aside. As the gas is absorbed by the carbonate of sodium, hydrochloric acid rises into the marble tube, and generates fresh gas, which, in its turn, drives back the acid liquid, and thus prevents the production of any more gas until further absorption has occurred. When the salt is wholly converted into bicarbonate ($NaHCO_3$), it will be found to have become damp through the liberation of water from the crystallized carbonate ($Na_2CO_3,10H_2O$). (It would be inconveniently moist, even semi-fluid, if a part of the carbonate had not previously been rendered anhydrous.) The *Sodii Bicarbonas*, U. S. P., is the commercial bicarbonate purified from any carbonate or traces of other salts by introducing it into a percolator and passing water through it till the washings cease to precipitate a solution of sulphate of magnesium, when the bicarbonate of sodium is removed from the percolator and dried on bibulous paper in a warm place.

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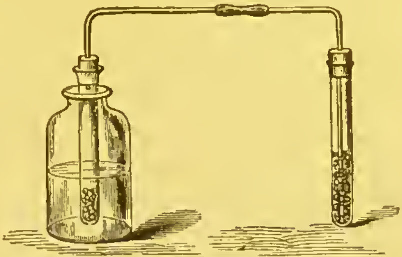
* The "water" alluded to occurs in the acid, which, though commonly termed "acetic" acid, is really a solution of that acid in water.

Fig 17.



Preparation of bicarbonate of sodium.

The carbonate of sodium may be placed, not in a test-tube or bottle, but in a vertical tube the bottom of which is loosely closed by a grooved cork. Any water of crystallization that is set free then runs off (into a basin or cup beneath), and takes with it any impurities (chlorides or sulphates, etc.) that may have been present in the original salt.

A *crystal* of carbonate of sodium is carbonate of sodium plus water (*Sodii Carbonas*, U. S. P.; see "Carbonates"); on heating it, more or less of the water is evolved, and *anhydrous* carbonate of sodium is partially or wholly produced (*Sodii Carbonas Exsiccatus*, U. S. P.).

$Na_2CO_3,10H_2O$	—	$10H_2O$	=	Na_2CO_3
Crystallized carbonate of sodium (286).		Water (180).		Dried carbonate of sodium (106).

According to the United States Pharmaeopœia dried carbonate of sodium is to be prepared by exposing crystals of carbonate of sodium to warm air for several days to effloresce, and then to a temperature of about 45° C. until half the original weight is obtained. 286 parts would thus become 143, and the latter would thus still retain 37 parts of water. In other words, the dried carbonate contains 72.6 per cent. of anhydrous carbonate and 27.4 per cent. of water. The crystals contain, obviously, a little more than 37 per cent. of anhydrous carbonate and nearly 63 per cent. of water. *The student should verify all these figures.*

Note on Nomenclature.—*Anhydrous* bodies (from *a*, *α*, and ὕδωρ, *hudōr*, i. e. without water) are compounds from which water has been taken, but whose essential chemical properties are unaltered. Salts containing water are *hydrous* bodies; of these the larger portion are crystalline, and their water is then termed *water of crystallization.* Non-crystalline *hydrous* compounds were formerly spoken of as *hydrated* substances; *hydrates* are, however, a distinct class of bodies, salts derived from water by one-half of its hydrogen becoming displaced by an equivalent quantity of another radical. *Anhydrides* form still another distinct class of chemical substances; they are derived from acids; in short, they are acids from which, not exactly water as water, but the elements of water have been removed, the essential chemical (acid) properties being thereby greatly altered. (For illustrations, see Index, "Anhydrides.")

Water of Crystallization.—The water in crystallized carbonate of sodium is in the solid condition, and, like ice and other fusible substances, requires heat for its liquefaction. Many salts (freezing-mixtures), when dissolved in water, give a very cold solution. This is because they and their solid water, if they have any, are then, absorbing some heat from surrounding media, converted into liquids. Take away from water some of its heat, the result is ice. Give to ice (at 32° F.) more heat than it contains already, the result is water (still at 32° F.). (Heat thus taken into a substance without increasing its temperature is said to become *latent*—from *latens*, hiding; it is no longer discoverable by the sense of touch or the thermometer. The term *latent* gives a somewhat incorrect idea, however, of the process; for our knowledge of the extent and readiness with which one form of force is convertible into another renders highly probable the assumption that heat is in these cases converted into motion, the latter enabling the molecules of a solid to take up the new positions demanded by their liquid condition.) The only apparent difference between ice and the water in such crystals as carbonate of sodium is that ice is solid water in the free, and water of crystallization solid water in the combined state. The former can only exist at and below 32° F.; the latter may exist at ordinary temperatures. Many salts, however, which unite with little or even no water of crystallization at common temperatures, take up much, according to Guthrie, at very low temperatures, and such salts he calls *cryohydrates* (χρυος, *kruos*, icy cold, frost). On the other hand, all water of crystallization is dispelled at high temperatures. In chemical formulæ, the symbols representing water are usually separated by a comma from those representing salts. The crystals of acetate of sodium (of the third reaction) contain water in this loose state of combination—water of crystallization ($NaC_2H_3O_2,3H_2O$).

"*Soda-water.*"—A solution of bicarbonate of sodium in water charged with carbonic acid gas under pressure constitutes the official *Liquor Sodæ Effervescens*, B. P., and, like the "potash-water" of the shops, is a true medicine, an antacid. Ordinary "soda-water," however, is in many cases simply a solution of carbonic acid gas in water, and would be more appropriately termed "aërated water:" any medicinal effect it may possess is due to the sedative influence of its carbonic acid gas on the coats of the stomach. At common temperatures water dissolves about its own volume of carbonic acid gas, both being under the same pressure. One pint of the official soda-water contains 30 grains of bicarbonate of sodium and a pint of carbonic acid gas; but the solution is under a pressure of seven atmospheres, so that seven pints of the gas at ordinary atmospheric pressure are required for the quantity mentioned.

Solubility of Gases in Water.—Whatever the weight and volume of a gas dissolved by a liquid at ordinary atmospheric pressure, that weight is doubled by double pressure, the two volumes of gas thereby being reduced to one, trebled at treble pressure, the three volumes of gas being reduced to one, quadrupled at quadruple pressure, the four volumes of gas being reduced to one, and so on. This is a general law (Henry and Dalton) regarding the solubility of gases in liquids under given temperatures. An average bottle of "soda-water" contains about four times the weight of carbonic acid gas which can exist in it without artificial pressure, so that on removing its cork three times its bulk escapes, its own bulk remaining dissolved.

Tartrate of Potassium and Sodium.

Fifth Synthetical Reaction.—To some hot strong solution of carbonate of sodium (about three parts) in a test-tube or larger vessel add acid tartrate of potassium (about four parts), till no more effervescence occurs; when the solution is cold, crystals of the tartrate of potassium and sodium (*Potassii et Sodii Tartras*, U. S. P.), the old *Rochelle Salt*, will be deposited—($KNaC_4H_4O_6,4H_2O$). The crystals are usually halves of right rhombic prisms.

Na_2CO_3	+	$2KHC_4H_4O_6$	=	$2KNaC_4H_4O_6$	+	H_2O	+	CO_2
Carbonate of sodium.		Acid tartrate of potassium.		Tartrate of potassium and sodium.		Water.		Carbonic acid gas.

FORMULÆ OF TARTRATES.

Tartaric acid	$HH\ C_4H_4O_6$
Acid tartrate of potassium	$KH\ C_4H_4O_6$
Tartrate of potassium and sodium . .	$KNaC_4H_4O_6$

Very close analogy will be noticed in the constitution of the molecules of these salts. When the other tartrates come under notice, it will be found they also have a similar constitution.

Hypochlorite of Sodium.

Liquor Sodæ Chloratæ, U. S. P., "Labbaraque's Solution," is made by decomposing solution of carbonate of sodium by solution of chlorinated lime; 100 parts of the carbonate, 80 of chlorinated lime, and 820 of water. Sp. gr. 1.044.

$$\underset{\text{Carbonate of sodium.}}{2Na_2CO_3} + \underset{\text{Chlorinated lime.}}{CaCl_2,Ca2ClO} = \underset{\text{Chlorinated soda.}}{2(NaCl,NaClO)} + \underset{\text{Carbonate of calcium.}}{2CaCO_3}$$

Other Sodium Compounds.

Synthetical Reactions portraying the chemistry of the remaining official compounds (namely, nitrate, sulphate, hyposulphite, borate, arseniate, and valerianate of sodium) are deferred until the several acidulous radicals of these salts have been described.

Phosphate of Sodium.—The preparation and composition of this salt will be most usefully studied after bone-ash, the source of it and other phosphates, has been described. Bone-ash is phosphate of calcium (see page 109).

The Citro-Tartrate (*Sodæ Citro-tartras Effervescens*, B. P.) is a mixture of bicarbonate of sodium (17 parts), citric acid (6), and tartaric acid (8), heated (to 200° or 220° F.) until the particles aggregate to a granular condition. When required for medicinal use, a dose of the mixture is placed in water; escape of carbonic acid gas at once occurs, and an effervescing liquid results. This substance may be regarded as the official representative of the popular "Effervescing Citrate of Magnesia," which will be further noticed in connection with the salts of magnesium (page 118).

Soda Powders are formed of 30 grains of bicarbonate of sodium and 25 of tartaric acid wrapped separately in papers of different color. When mixed with water, tartrate of sodium results, a little bicarbonate also remaining.

In the manufacture of Carbonate of Sodium from chloride, the source of the sodium is chloride of sodium, and of the carbonic radical carbonate of calcium in the form of limestone. The chloride is first converted into sulphate, the sulphate is then roasted with coal and limestone, and the resulting *black-ash* lixiviated (*lixivia*, from *lix*, lye—water impregnated with alkaline salts: hence *lixiviation*, the operation of washing a mixture with the view of dissolving out salts). The lye, evaporated to dryness, yields crude carbonate of sodium (soda-ash). This process will be further described in connection with Carbonates.

Deliquescence and Efflorescence.—The carbonates of sodium and potassium, chemically closely allied, are readily distinguished physically. Carbonate of potassium quickly absorbs moisture from the air and becomes damp, wet, and finally fluid—it is *deliquescent* (*deliquescens*, melting away). Carbonate of sodium, on the other hand, yields some of its water of crystallization to the air, the crystals becoming white, opaque, and pulverulent—it is *efflorescent* (*efflorescens*, blossoming forth).

Analogy of Sodium Salts to Potassium Salts.—Other synthetical reactions might be described similar to those given under potassium, and thus citrate, iodide (*Sodii Iodidum*, U. S. P.), NaI, bromide (*Sodii Bromidum*, U. S. P.), NaBr, iodate, bromate, chlorate (*Sodii Chloras*, U. S. P.), $NaClO_3$, manganate and permanganate of sodium, and many other salts be formed. But enough has been stated to show how analogous sodium is chemically to potassium. Such analogies will constantly present themselves. In few departments of knowledge are order and method more perceptible; in few is there as much natural law, as much *science*, as in chemistry.

Substitution of Potassium and Sodium Salts for each other.—Sodium salts being cheaper than potassium salts, the former may sometimes be economically substitued. That one is employed rather than the other, is often merely a result due to accident or fashion. But it must be borne in mind that in some cases a potassium salt will crystallize more readily than its sodium analogue, or that a sodium salt is stable when the corresponding potassium salt has a tendency to absorb moisture, or one may be more soluble than the other, or the two may have different medicinal effect. For these or similar reasons, a potassium salt has come to be used in medicine or trade, instead of the corresponding sodium salt, and *vice versâ*. Whenever the acidulous portion only is to be utilized, the least expensive salt of the class would nearly always be selected.

(*b*) *Reactions having Analytical Interest.*

1. *The chief analytical reaction* for sodium is the *flame-test*. When brought into contact with a flame in the manner described under potassium (page 79), an intensely yellow color is communicated to the flame by any salt of sodium. This is highly characteristic—indeed, almost too delicate a test; for if the point of the wire be touched by the fingers, enough salt (which is contained in the moisture of the hand) adheres to the wire to communicate a very distinct sodium reaction. These statements should be experimentally verified, the chloride, sulphate, or any other salt of sodium being employed.

2. *Precipitant of Sodium.*—Sodium is the only metal whose common salts are all soluble in water. Hence no ordinary reagent can be added to a solution containing a sodium salt which shall give a precipitate containing the sodium. A neutral or alkaline solution of a sodium salt gives, however, a granular precipitate of antimoniate of sodium ($Na_2H_2Sb_2O_7,6H_2O$) if well stirred or shaken with a solution of *antimoniate of potassium* ($K_2H_2Sb_2O_7$), but the reagent precipitates other metals, and is liable to decompose and become useless, and hence is seldom employed.

Antimoniate of potassium is made by adding, gradually, finely powdered metallic antimony to nitrate of potassium fused in a crucible so long as deflagration continues. The resulting mass is boiled with a large quantity of water, the solution filtered and preserved in a well-stoppered bottle; for the carbonic gas in the air is rapidly absorbed by the solution, antimonic acid being deposited.

3. Sodium salts, like those of potassium, are not volatile. Prove this fact by the means described when treating of the effect of heat on potassium salts (p. 79).

QUESTIONS AND EXERCISES.

98. How is the official Solution of Soda prepared? Give a diagram or equation.

99. Explain the action of sodium or potassium on water. What colors do these elements respectively communicate to flame?

100. How much bicarbonate of sodium can be obtained from 2240 pounds of crystallized carbonate of sodium? Ans. 1316 lbs., nearly.

101. Acetate of Sodium: give formula, process, and equation.

102. Give a diagram showing the formation of Bicarbonate of Sodium.

103. Why is a mixture of dried and undried carbonate of sodium employed in the preparation of the bicarbonate?

104. State the difference between anhydrous and crystallized carbonate of sodium.

105. Define the terms *anhydrous*, *hydrous*, *hydrate*, *anhydride*.

106. What do you understand by *water of crystallization?*

107. What is the nature of "Soda-water"?

108. How many volumes of gas (reckoned as at ordinary atmospheric pressure) are contained in any given volume of the British official "Soda-water"?

109. What is the general law regarding the solubility of gases in liquids under pressure?

110. What is the systematic name of Rochelle salt, and how is the salt prepared?

111. What is the relation of Rochelle salt to cream of tartar and tartaric acid?

112. Give the mode of preparation and composition of Solution of Chlorinated Soda, and express the process by a diagram.

113. How is the granular effervescing Citro-tartrate of Sodium prepared?

114. Define *Deliquescence*, *Efflorescence*, and *Lixiviation*.

115. What is the general relation of potassium salts to those of sodium?

116. How are sodium salts analytically distinguished from those of potassium?

AMMONIUM.

Symbol NH_4 or Am. Atomic weight 18.

Memoranda.—The elements nitrogen and hydrogen, in the proportion of one atom to four (NH_4), are those characteristic of all the compounds about to be studied, just as potassium (K) and sodium (Na) are the characteristic elements of the potassium and sodium compounds. Ammonium is a univalent nucleus, root, or radical, like potassium or sodium; and the ammonium compounds closely resemble those of potassium or sodium. In short, if, for an instant, potassium or sodium be imagined to be compounds, the analogy between these three series of salts is complete. Ammonium is said to have been isolated by Weyl, as an unstable dark-blue liquid possessing a metallic lustre.

Source.—The source of nearly all the ammoniacal salts met with in commerce is ammonia-gas (NH_3) obtained in distilling coals in the manufacture of ordinary illuminating gas and of coke. It is doubtless derived from the nitrogen of the plants from which the coal has been produced. It is possible, however, to produce ammonia from its elements. Thus, coal-dust, air, and vapor of water, all at a red heat, yield, according to Rickman and Thompson, gaseous ammonia. Salt added to the mixture prevents the further combustion of the formed ammonia, and chloride of ammonium sublimes. Nitrogen and hydrogen passed over spongy platinum yields traces of ammonia.

Ammonia.—When this gas (NH_3) comes into contact with water (H_2O), in the process of washing and cooling coal-gas, hydrate of ammonium (NH_4HO, or $AmHO$) is believed to be formed, the analogue of hydrate of potassium (KHO) or sodium ($NaHO$). The grounds for this belief are the observed analogy of the well-known ammoniacal salts to those of potassium and sodium, the similarity of action of solution of potash, soda, and ammonia on salts of most metals, and the existence of crystals of an analogous sulphur salt (NH_4HS).

Chloride of Ammonium.—The "ammoniacal liquor" of the gas-works is usually neutralized by hydrochloric acid, by which crude *chloride of ammonium* (sal-ammoniac) is produced.

$$NH_4HO + HCl = NH_4Cl + H_2O\ ;$$

and from this salt, purified, the others used in pharmacy are directly or indirectly made. Chloride of ammonium (*Ammonii Chloridum*, U. S. P.) occurs in colorless, inodorous, translucent fibrous masses, tough, and difficult to powder, and as a snow-white crystalline powder, soluble in water [1 in 10 is the "Solution of Chloride of Ammonium," U. S. P.] and in rectified spirit. Chloride of ammonium generally contains slight traces of oxychloride of iron, tarry matter, and possibly chlorides of compound ammoniums (*vide* "Artificial Alkaloids" in Index).

Sulphate of Ammonium, $(NH_4)_2SO_4$, results when "ammoniacal liquor" is neutralized by oil of vitriol. It is largely used as a constituent of artificial manure in England, and when purified by recrystallization is employed in pharmacy (*Ammonii Sulphas*, U. S. P.).

Volcanic Ammonia.—A very pure form of ammonia is that met with in volcanic districts, and obtained as a by-product in the manufacture of borax; the crude boracic acid as imported contains from 5 to 10 per cent. of ammonium salts, chiefly sulphate, and double sulphates of ammonium with magnesium, sodium, and manganese (Howard).

Reactions having (*a*) General, (*b*) Synthetical, and (*c*) Analytical Interest.

Ammonium-Amalgam. (?)

(*a*) *General Reaction.*—To forty or fifty grains of dry mercury in a *dry* test-tube, add one or two small pieces of sodium (freed from adhering naphtha by gentle pressure with a piece of filter-paper), and amalgamate by gently warming the tube. To this amalgam, when cold, add some fragments of chloride of ammonium and a strong solution of the same salt. The sodium amalgam soon begins to swell and rapidly increase in bulk, probably overflowing the tube. The light spongy mass produced is the so-called ammonium-amalgam, and the reaction is usually adduced as evidence of the existence of ammonium; the sodium of the amalgam unites with the chlorine of the chloride of ammonium, while the ammonium is supposed to form an amalgam with the mercury. As soon as formed the amalgam gives off hydrogen and ammonia gases; this decomposition is nearly complete after some minutes, and impure mercury remains.

(*b*) *Reactions having Synthetical Interest.*

Hydrate of Ammonium. Ammonia.

First Synthetical Reaction.—Heat a few grains of sal-ammoniac with about an equal weight of hydrate of calcium (slaked lime) dampened with a little water in a test-tube; ammonia gas is given off, and may be recognized by its well-known odor. It is very soluble in water. Pass a delivery-tube, fitted to the test-tube as described for the preparation of oxygen and hydrogen, into a second test-tube, at the bottom of which is a little water; again heat, the end of the delivery-tube being only just beneath the surface of the water (or, possibly, all the water might rush into the generating-tubes, water absorbing ammonia gas with great avidity); solution of ammonia will be thus formed.

$$\underset{\substack{\text{Chloride of}\\ \text{ammonium.}}}{2NH_4Cl} + \underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{CaCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Ammonia}\\ \text{gas.}}}{2NH_3}$$

Ammonia gas is composed of one atom of nitrogen with three atoms of hydrogen; its formula is NH_3; two volumes of it contain one volume of nitrogen combined with three atoms or volumes of hydrogen. Its constituents have therefore in combining suffered condensation to one half their normal bulk. Its conversion into hydrate of ammonium may be thus shown:—

$$\underset{\text{Ammonia gas.}}{NH_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hydrate of ammonium (ammonia).}}{NH_4HO \text{ or } AmHO}$$

Solutions of Ammonia, prepared by this process on a large scale and in suitable apparatus, are met with in pharmacy—the one (sp. gr. 0.900) containing 28 per cent., the other (sp. gr. 0.959), 10 per cent., by weight, of ammonia gas, NH_3 (*Aqua Ammoniæ Fortior* and *Aqua Ammoniæ*, U. S. P.). On the large scale, bottles are so arranged in a series as to condense all the ammonia evolved during the operation.

Acetate of Ammonium.

Second Synthetical Reaction.—To acetic acid and water in a test-tube, add powdered commercial carbonate (acid carbonate and carbamate) of ammonium till effervescence ceases; the resulting liquid, made of prescribed strength, is the official solution of Acetate of Ammonium ($NH_4C_2H_3O_2$) (*Liquor Ammonii Acetatis*, U. S. P.), the old "Spirit of Mindererus."

$$\underset{\text{Acid carbonate and carbamate of ammonium.}}{NH_4HCO_3, NH_4NH_2CO_2} + \underset{\text{Acetic acid.}}{3HC_2H_3O_2} = \underset{\text{Acetate of ammonium.}}{3NH_4C_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Carbonates of Ammonium.

Commercial carbonate of ammonium is made by heating a mixture of chalk and sal-ammoniac; chloride of calcium ($CaCl_2$) is produced, ammonia gas (NH_3) and water (H_2O) escape, and the ammoniacal carbonate distils, or rather sublimes,* in cakes (*Ammonii Carbonas*, U. S. P.). The best form of apparatus to employ is a retort with a short wide neck and a cool receiver. On the large scale the retort is usually iron and the receiver earthenware or glass; on the small scale glass vessels are employed. The salt is purified by resublimation at a low temperature; 150° F. is said to be sufficient.

This salt, the empirical formula of which is $N_3H_{11}C_2O_5$, is probably a mixture of one molecule of acid carbonate or bicarbonate of ammonium (NH_4HCO_3) and one of a salt termed carbamate of ammonium ($NH_4NH_2CO_2$). The latter belongs to an important class of salts known as carbamates, but it is the only one of interest to the pharmacist. Cold water extracts it from the commercial carbonate of ammonium, leaving the acid carbonate of ammonium undissolved, if the amount of liquid used be very small. Alcohol extracts the carbamate, leaving the acid carbonate undissolved. In water, carbamate soon changes into neutral carbonate of ammonium,

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* *Sublimation* (from *sublimis*, high). Vaporization of a solid substance by heat, and its condensation on an upper and cooler part of the vessel or apparatus in which the operation is performed.

$$NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3 \text{ or } Am_2CO_3;$$

so that an aqueous solution of commercial carbonate of ammonium contains both acid carbonate and neutral carbonate of ammonium. If to such a solution some ordinary solution of ammonia be added, a solution of *neutral carbonate of ammonium* is obtained; and this is the common reagent always found on the shelves of the analytical laboratory.

$$AmHCO_3 + AmHO = Am_2CO_3 + H_2O.$$

Neutral carbonate of ammonium is the salt formed on adding strong solution of ammonia to the the commercial carbonate in preparing a pungent mixture for toilet smelling-bottles; but it is unstable, and on continued exposure to air is reduced to a mass of crystals of the acid carbonate or bicarbonate of ammonium. Bicarbonate of ammonium (NH_4HCO_3) is also produced on passing carbonic acid gas into an aqueous solution of commercial carbonate.

According to Divers, the sublimed product of the first distillation of chalk and sal-ammoniac is a mixture of carbamate and carbonate of ammonium, the latter losing some ammonia gas on redistillation, and carbamate with bicarbonate forming the resulting commercial salt.

If carbonate of ammonium contain more than traces of empyreumatic matters (derived primarily from the gas-liquors), an aqueous solution, with excess of sulphuric acid added, will decolorize a dilute solution of permanganate of potassium at once.

Sal Volatile (*Spiritus Ammoniæ Aromaticus*, U. S. P.) is a spirituous solution of ammonia ($AmHO$), neutral carbonate of ammonium (Am_2CO_3), and the oils of lemon, lavender and pimenta. Fetid spirit of ammonia (*Spiritus Ammoniæ Fœtidus*, B. P.) is an alcoholic solution of the volatile oil of asafœtida mixed with solution of ammonia. "Solution of Carbonate of Ammonia," B. P., is formed by dissolving 1 part of the salt in 10 of water. *Spiritus Ammoniæ*, U. S. P., is an alcoholic solution of ammonia containing 10 per cent., by weight, of gas (NH_3).

Nitrate of Ammonium.

Third Synthetical Reaction.—To some diluted nitric acid add carbonate of ammonium, until, after well stirring, a slight ammoniacal odor remains. The solution contains Nitrate of Ammonium (*Ammonii Nitras*, U. S. P.)

$NH_4HCO_3, NH_4NH_2CO_2$	$+$	$3HNO_3$	$=$	$3NH_4NO_3$	$+$	H_2O	$+$	$2CO$
Acid carbonate and carbamate of ammonium.		Nitric acid.		Nitrate of ammonium.		Water.		Carbonic acid gas.

From a strong hot solution of nitrate of ammonium crystals may be obtained containing much water (NH_4NO_3, $12H_2O$). On heating these to about 310° F. the water escapes. The anhydrous salt remaining (NH_4NO_3) may be poured on to an iron plate. On further heating the powdered nitrate, it is resolved into *nitrous oxide* gas (the so-called laughing gas) and water.

$$NH_4NO_3 = N_2O + 2H_2O.$$

Nitrous oxide is thus prepared for use as an anæsthetic. When required for inhalation, it should be washed from any possible trace of acid or nitric oxide, by being passed through solution of potash, and through solution of ferrous sulphate.

Nitrous oxide is slightly soluble in warm water, more so in cold. It supports combustion almost as well as oxygen. By pressure it may be liquefied to a colorless fluid, and by simultaneous cooling solidified.

Citrate, Phosphate, and Benzoate of Ammonium.

Fourth Synthetical Reaction. To solution of citric acid ($H_3C_6H_5O_7$ or H_3Ci) add solution of ammonia ($AmHO$) until the well-stirred liquid smells faintly of ammonia; the product is Solution of Citrate of Ammonium (Am_3Ci) (*Liquor Ammoniæ Citratis*, B. P.).

Phosphate of Ammonium (Am_2HPO_4) (*Ammonii Phosphas*, U. S. P.) and *Benzoate of Ammonium* ($AmC_7H_5O_2$) (*Ammonii Benzoas*, U. S. P.) are also made by adding solution of ammonia to phosphoric acid (H_3PO_4) and benzoic acid ($HC_7H_5O_2$) respectively, evaporating (keeping the ammonia in slight excess by adding more of its solution), and setting aside for crystals to form. The official Solution of Acetate of Ammonium could be made in the same way; but, when prepared with Carbonate of Ammonium, the liquid remains charged with carbonic acid, and has a less vapid flavor.

$$\underset{\text{Citric acid.}}{H_3C_6H_5O_7} + \underset{\text{Ammonia.}}{3AmHO} = \underset{\text{Citrate of ammonium.}}{Am_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Phosphoric acid.}}{H_3PO_4} + \underset{\text{Ammonia.}}{2AmHO} = \underset{\text{Phosphate of ammonium.}}{Am_2HPO_4} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\text{Benzoic acid.}}{HC_7H_5O_2} + \underset{\text{Ammonia.}}{AmHO} = \underset{\text{Benzoate of ammonium.}}{AmC_7H_5O_2} + \underset{\text{Water.}}{H_2O}$$

Phosphate of ammonium occurs in transparent colorless prisms, soluble in water, insoluble in spirit; benzoate in crystalline plates, soluble in water and in spirit.

Ammonii Iodidum, U. S. P., may be made by decomposing the two bodies iodide of potassium and sulphate of ammonium, which give iodide of ammonium and sulphate of potassium; the latter salt is separated by adding alcohol to the cooled solution, when, by reason of its insolubility in alcohol, it crystallizes out, and the separated solution of iodide of ammonium is then evaporated to dryness. It occurs usually in minute white crystalline cubes.

Bromide of Ammonium (*Ammonii Bromidum*, U. S. P.) will be noticed in connection with Hydrobromic Acid and other Bromides.

Oxalate of Ammonium.

Fifth Synthetical Reaction.—To a nearly boiling solution of 1 part of oxalic acid in about 8 of water add carbonate of ammonium until the liquid is neutral to *test-paper* (see following paragraph), filter while hot, and set aside for crystals ($(NH_4)_2C_2O_4,H_2O$) to form. The mother-liquor is useful as a reagent in analysis; 1 of the salt in 20 of water constitutes "Solution of Oxalate of Ammonium," U. S. P.

$$\underset{\text{Oxalic acid.}}{3H_2C_2O_4} + \underset{\text{Carbonate of ammonium.}}{2N_3H_{11}C_2O_5} = \underset{\text{Oxalate of ammonium.}}{3(NH_4)_2C_2O_4} + \underset{\text{Carbonic acid gas.}}{3CO_2} + \underset{\text{Water.}}{2H_2O}$$

Neutralization.—Thus far, in reactions, the student has avoided excess of either acid matter on the one hand, or alkaline matter on the other, by the rough aid of taste, cessation of effervescence, presence or absence of odor, etc. More delicate aid is afforded by *test-papers.*

Test-papers.—*Litmus* is a blue vegetable pigment, prepared from various species of *Roccella* lichen, exceedingly sensitive to the action of acids, which turn it red. When thus reddened, alkalies (potash, soda, and ammonia) and other soluble hydrates readily turn it blue. The student should here test for himself the delicacy of this action by experiments with paper soaked in solution of litmus and dipped into very dilute solutions of acids, acid salts ($KHC_4H_4O_6$, *e. g.*), alkalies, and such neutral salts as nitrate of potassium, sulphate of sodium, or chloride of ammonium.

Solution of Litmus (U. S. P.).—1 part of litmus is macerated for seven days in 10 parts of diluted alcohol, and the solution poured off from insoluble matter.

Blue litmus paper (U. S. P.) is "unsized white paper colored with solution of litmus." *Red litmus paper* (U. S. P.) is "unsized white paper colored with solution of litmus previously reddened by the smallest requisite quantity of sulphuric acid."

Turmeric paper (U. S. P.), similarly prepared from tincture of turmeric (1 of turmeric root or rhizome to 6 of diluted alcohol, macerated for seven days), is occasionally useful as a test for alkalies, which turn its yellow to brown; acids do not affect it.

Sulphydrate of Ammonium.

Sixth Synthetical Reaction.—Pass sulphuretted hydrogen gas (H_2S) through a small quantity of solution of ammonia in a test-tube, until a portion of the liquid no longer causes a white precipitate in solution of sulphate of magnesium (Epsom salt); the product is solution of sulphydrate (or sulphide) of ammonium (NH_4HS), the "Solution of Sulphide of Ammonium," U. S. P., a most valuable chemical reagent, as will presently be apparent.

$$NH_4HO + H_2S = NH_4HS + H_2O.$$

"*Test-Solution of Sulphide of Ammonium*," U. S. P., is made by passing the gas prepared in the apparatus described below into 3 fluidounces of Water of Ammonia so long as the gas continues to be absorbed, then adding 2 more ounces of the ammonia, and preserving the solution in a well-stoppered bottle.

Sulphuretted hydrogen is a compound of noxious odor; hence the above operation, and many others, described further on, in which this gas is indispensable, can only be performed in the open air, or in a fume-cupboard, a chamber so contrived that deleterious gases and vapors shall escape into a chimney in connection with the external air. In the above experiment, the small quantity of gas required can be made in a test-tube, after the manner of hydrogen itself. To two or three fragments of sulphide of iron (FeS), add water and then sulphuric acid; the gas is at once evolved, and may be conducted by a tube into the solution of Ammonia. Sulphate of iron remains dissolved in the water.

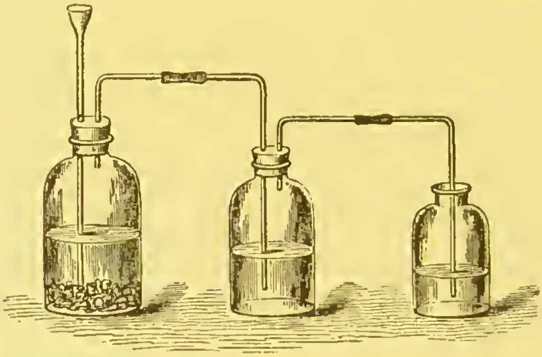
$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

Crystals of sulphydrate of ammonium (NH_4HS) may be obtained on bringing ammonia gas (NH_3) and sulphuretted hydrogen (H_2S) together at a low temperature. They are soluble in water without decomposition.

Sulphuretted-Hydrogen Apparatus.—As no heat is necessary in making sulphuretted hydrogen, the test-tube of the foregoing operation may be advantageously replaced by a bottle, especially when larger quantities of the gas are required. In analytical operations the gas should be purified by passing it through water contained in a second bottle.

The most convenient arrangement for experimental use is prepared as follows: Two common wide-mouthed bottles are selected, the one having a capacity of about half a pint, the other a quarter pint; the former may be called the generating-bottle, the latter the wash-bottle. Fit two corks to the bottles. Through each cork bore two holes by a round file or other instrument of such a size that glass tubing of about the diameter of a quill pen shall fit them tightly. Through one of the holes in the cork of the generating-bottle pass a funnel-tube, so that its extremity may nearly reach the bottom of the bottle. To the other hole adapt a piece of tubing, 6 inches long, and bent in the middle to a right angle. A similar "elbow-tube" is fitted to one of the holes in the cork of the wash-bottle, and another elbow-tube, one arm of which is long enough to reach to near the bottom of the wash-bottle, fitted to the other hole. Removing the corks, two or three ounces of water are now poured into each bottle, an ounce or two of sulphide of iron put into the generating-bottle, and the corks replaced. The elbow-tube of the generating-bottle is now attached by a short piece of India-rubber tubing to the long-armed elbow-tube of the wash-bottle, so that gas coming from the generator may pass through the water in the wash-bottle. The delivery-tube of the wash-bottle is then lengthened by attaching to it, by India-rubber tubing, another piece of glass tubing several inches in length. The apparatus is now ready for use. Strong sulphuric acid is poured down the funnel-tube in small quantities at a time, until brisk effervescence is established, and more added from time to time as the evolution of gas becomes slow. The gas passes through the tubes into the wash-bottle, where, as it bubbles up through the water, any trace of sulphuric acid, or other matter mechanically carried over, is arrested, and thence the gas flows out at the delivery-tube into any vessel or liquid that may be placed there to receive it. The generator must be occasionally dismounted and the sulphate of iron washed out.

Fig. 18.



Sulphuretted-Hydrogen Apparatus.

Luting (*lutum*, mud).—If the corks of the above apparatus are sound, and tube-holes well made, no escape of gas will occur. If rough corks have been employed, or the holes are not cylindrical, linseed-meal lute may be rubbed over the defective parts. The lute is prepared by mixing linseed-meal with water to the consistence of dough. A neat appearance may be given to the lute by gently rubbing a well-wetted finger over its surface.

(c) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—To a solution of any salt of ammonium (the chloride, for example) in a test-tube, add solution of caustic soda (or solution of potash, or a little slaked lime);

ammonia gas is at once evolved, recognized by its well-known odor.

$$NH_4Cl + NaHO = NH_3 + H_2O + NaCl.$$

Though ammonium itself cannot be kept in the free state, its compounds are stable. Ammonia is easily expelled from these compounds by action of the stronger alkalies, caustic potash, soda, or lime. As a matter of exercise, the student should here draw out equations in which acetate ($NH_4C_2H_3O_2$), sulphate (Am_2SO_4), nitrate (NH_4NO_3) or any other ammoniacal salt not already having the odor of ammonia, is supposed to be under examination; also representing the use of the other hydrates, potash (KHO) or slaked lime ($Ca2HO$).

The *odor* of ammonia gas is perhaps the best means of recognizing its presence; but the following tests are also occasionally useful. Into the test-tube in which the ammonia gas is evolved insert a glass rod moistened with hydrochloric acid (that is, with the solution of hydrochloric acid gas, conveniently termed hydrochloric acid, the *Acidum Hydrochloricum* of the Pharmacopœias); white fumes of chloride of ammonium will be produced.

$$NH_3 + HCl = NH_4Cl.$$

Hold a piece of moistened red litmus paper in a tube in which ammonia gas is present; the red color will be changed to blue.

Second Analytical Reaction.—To a few drops of a solution of an ammonium salt add a drop or two of hydrochloric acid and a like small quantity of solution of perchloride of platinum ($PtCl_4$); a yellow crystalline precipitate of the double chloride of platinum and ammonium ($PtCl_4 2NH_4Cl$) will be produced, similar in appearance to the corresponding salt of potassium, the remarks concerning which (p. 78) are equally applicable to the precipitate under notice.

Third Analytical Reaction.—To a moderately strong solution of an ammonium salt add a strong solution of tartaric acid, and shake or well stir the mixture; a white granular precipitate of acid tartrate of ammonium will be formed.

For data from which to draw out an equation representing this action, see the remarks and formulæ under the analogous salt of potassium (p. 77).

Fourth Analytical Fact.—Evaporate a few drops of a solution of an ammonium salt to dryness, or place a fragment of a salt in the solid state on a piece of platinum foil, and heat in a flame; the salt is readily *volatilized*. As already noticed, the salts of potassium and sodium are *fixed* under these circumstances, a point of difference of which advantage will frequently be taken in analysis. A porcelain crucible may often be advantageously substituted for platinum foil in experiments on volatilization.

Salts of ammonium with the more complex acidulous radicals seldom volatilize unchanged when heated. The oxalate, when warmed, loses its water of crystallization, and at a higher temperature decomposes, yielding carbonic oxide, carbonic acid gas, ammonia gas, water (the three latter sometimes in combination), and several organic substances. The phosphate yields more or less phosphoric acid as a residue.

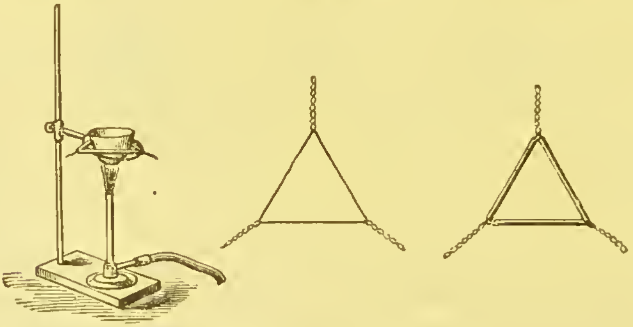


Fig. 19. Fig. 20. Fig. 21.

Triangular Supports for Crucibles.

A wire triangle may be used in supporting crucibles. It is made by twisting together each pair of ends of three (5 or 6 inch) crossed pieces of wire (Fig. 20). A piece of tobacco-pipe stem (about 2 inches) is sometimes placed in the centre of each wire before twisting, the transference of any metallic matter to the sides of the crucible being thus prevented (Fig. 21).

Practical Analysis.

With regard to those experiments which are useful rather as means of detecting the presence of potassium, sodium, and ammonium, than as illustrating the preparation of salts, the student should proceed to apply them to certain solutions of any of the salts of potassium, sodium, and ammonium, with the view of ascertaining which metal is present; that is, proceed to practical analysis.* A little thought will enable him to apply these reactions in the most suitable order and to the best advantage for the contemplated purpose: but the following arrangements are perhaps as good as can be devised:—

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* Such solutions are prepared in educational laboratories by a tutor. They should, under other circumstances, be mixed by a friend, as it is not desirable to know previously what is contained in the substance about to be analyzed.

The analysis of solutions containing only one salt serves to impress the memory with the characteristic tests for the various metals and other radicals, and familiarize the mind with chemical principles.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF **ONE** OF THE METALS, POTASSIUM, SODIUM, AMMONIUM.

Add caustic soda to a small portion of the solution to be examined, and warm the mixture in a test-tube; the odor of ammonia gas at once reveals the presence of an ammonium salt.

If ammonium be not present, apply the perchloride-of-platinum test to another portion of the liquid; a yellow precipitate proves the presence of potassium.

(It will be observed that potassium can only be detected in the absence of ammonium, salts of the latter radical giving similar precipitates.)

The flame-test is sufficient for the recognition of sodium.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF **ONE, TWO, OR ALL THREE** OF THE ALKALI METALS.

Commence by testing a small portion of the solution for an ammonium salt. If present, make a memorandum to that effect, and then proceed to get rid of the ammoniacal compound to make way for the detection of potassium: advantage is here taken of the volatility of ammonium salts and the fixity of those of potassium and sodium. Evaporate the original solution to dryness in a small basin, transfer the solid residue to a porcelain crucible, and heat the latter to a low redness, or until dense white fumes (of ammoniacal salts) cease to escape. (See Fig. 19.) This operation should be conducted in a fume-cupboard, to avoid contamination of the air of the apartment. When the crucible is cold, dissolve out the solid residue with a small quantity of hot water, and test the solution for potassium by

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Medical students seldom have time to go further than this. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of bodies as are met with in actual practice, beginning with solutions which may contain any or all the members of a group. Hence in this Manual two Tables of short directions for analyzing are given under each group. Pharmaceutical students should follow the second Table.

the perchloride-of-platinum test, and for sodium by the flame-test.

If ammonium is proved to be absent, the original solution may, of course, be at once tested for potassium and sodium.

Flame-test.—The violet tint imparted to flame by potassium salts may be seen when masked by the intense yellow color due to sodium, if the flame be observed through a piece of dark-blue glass, a medium which absorbs the yellow rays of light.

Note on Nomenclature.—The operations of *evaporation* and heating to redness, or *ignition*, are frequently necessary in analysis, and are usually conducted in the above manner. If vegetable or animal matter be also present, carbon is set free, and ignition is accompanied by *carbonization;* the material is said to *char.* When all carbonaceous matter is burnt off, the crucible being slightly inclined and its cover removed to facilitate combustion, and mineral matter, or *ash*, alone remains, the operation of *incineration* has been effected.

Note on the Classification of Elements.—The compounds of potassium, sodium, and ammonium have many analogies. Their carbonates, phosphates, and other common salts are soluble in water. The atoms of the radicals themselves are univalent—that is, displace or are displaced by one atom of hydrogen. In fact, they constitute by their similarity in properties a distinct group or family. All the elements thus naturally fall into classes—a fact that should constantly be borne in mind, and evidence of which should always be sought. It would be impossible for the memory to retain the details of chemistry without a system of classification and leading principles. Classification is also an important feature in the art as well as in the science of chemistry; for without it practical analysis could not be undertaken. The classification adopted in this volume is founded on the quantivalence of the elements and on their analytical relations.

QUESTIONS AND EXERCISES.

117. Why are ammoniacal salts classed with those of potassium and sodium?

118. Mention the sources of the ammonium salts.

119. Describe the appearance and other characters of Chloride of Ammonium.

120. Give the formula of Sulphate of Ammonium.

121. Adduce evidence of the existence of ammonium.

122. How are the official Waters of Ammonia prepared? Give diagrams.

123. How is the official Solution of Acetate of Ammonium prepared?

124. What is the composition of commercial Carbonate of Ammonium?

125. Define *sublimation.*

126. What ammoniacal salts are contained in *Spiritus Ammoniæ Aromaticus?*

127. Give diagrams or equations illustrating the formation of Citrate, Phosphate, and Benzoate of Ammonium?

128. Give the formula of Oxalate of Ammonium.

129. Show how Hydrate of Ammonium may be converted into Sulphydrate.

130. Describe the preparation of Sulphuretted Hydrogen gas.

131. Enumerate and explain the tests for ammonium.

132. How is potassium detected in a solution in which ammonium has been found?

133. Give equations illustrating the action of hydrate of sodium on acetate of ammonium; hydrate of potassium on sulphate of ammonium; and hydrate of calcium on nitrate of ammonium.

134. What are the effects of acids and alkalies on litmus and turmeric?

135. Describe the analysis of an aqueous liquid containing salts of potassium, sodium, and ammonium.

136. What meanings are commonly assigned to the terms *evaporation*, *ignition*, *carbonization*, and *incineration?*

137. Write a short article descriptive of the analogies of potassium, sodium, and ammonium, and their compounds.

BARIUM, CALCIUM, MAGNESIUM.

These three elements have many analogies. Their atoms are bivalent.

BARIUM.

Symbol Ba. Atomic weight 136.8.

The analytical reactions only of this metal are of interest to the general student of pharmacy. The nitrate ($Ba2NO_3$) and chloride ($BaCl_2,2H_2O$) are the soluble salts in common use in analysis ("Test-Solution of Chloride of Barium," 1 in 10 of water, U. S. P.); and these and others are made by dissolving the native carbonate ($BaCO_3$), the mineral *witherite*, in acids, or by heating the other common natural compound of barium, the sulphate, *heavy white* or *heavy spar* ($BaSO_4$), with coal, which yields sulphide of barium (BaS),

$$BaSO_4 + C_4 = 4CO + BaS,$$

and dissolving the sulphide in appropriate acids. When the nitrate is strongly heated, it is decomposed, the oxide of barium or *baryta* (BaO) remaining. Baryta, on being moistened, assimilates the elements of water with great avidity, and yields hydrate of barium ($Ba2HO$). The latter is tolerably soluble, giving *baryta-water;* and from this solution crystals of hydrate of barium are obtained on evaporation.

The operations above described may all be performed in test-tubes and small porcelain crucibles heated by the gas-flame. Quantities of 1 oz. to 1 lb. require a coke-furnace.

Peroxide of barium (BaO_2) is formed on passing air over baryta heated to low redness. By the action of dilute hydrochloric acid it yields solution of *peroxide of hydrogen* (H_2O_2), the old *oxygenated water.*

Quantivalence.—The atom of barium is bivalent, Ba''.

Reactions having Analytical Interest (Tests).

First Analytical Reaction.—To the aqueous solution of any soluble salt of barium (nitrate or chloride, for example) add dilute sulphuric acid; a white precipitate is obtained. Set the test-tube aside for two or three minutes, and when some of the precipitate has fallen to the bottom pour away the supernatant liquid; wash the precipitate by adding water, shaking, setting aside, and again decanting; then add strong nitric acid, and boil; the precipitate is insoluble.

The production of a white precipitate by sulphuric acid, insoluble even in hot nitric acid, is highly characteristic of barium. The name of this precipitate is sulphate of barium; its formula is $BaSO_4$.

Antidotes.—In cases of poisoning by soluble barium salts, obvious antidotes would be solutions of alum or of any sulphates, such as those of magnesium and sodium (Epsom salt, Glauber's salt).

Second Analytical Reaction.—To a barium solution add solution of the yellow chromate of potassium (K_2CrO_4); a pale yellow precipitate ($BaCrO_4$) falls. Add acetic acid to a portion of the chromate of barium; it is insoluble. Add hydrochloric or nitric acid to another portion; it is soluble.

"*Neutral Chromate.*"—The red chromate (or bichromate) of potassium (K_2CrO_4,CrO_3) must not be used in this reaction, or the barium will be only imperfectly precipitated; for the red salt gives rise to the formation of free acid, in which chromate of barium is to some extent soluble:—

$$K_2CrO_4,CrO_3 + 2BaCl_2 + H_2O = 2BaCrO_4 + 2KCl + 2HCl.$$

Yellow chromate is obtained on adding carbonate of potassium, in small quantities at a time, to a hot solution of the red chromate until effervescence ceases; a little more red chromate is then added to ensure decomposition of any slight excess of carbonate of potassium.

$$K_2CrO_4,CrO_3 + K_2CO_3 = 2K_2CrO_4 + CO_2.$$

For analytical purposes, solution of a neutral chromate is still more readily prepared by simply adding solution of ammonia to solution of red chromate of potassium, until the liquid turns yellow, and, after stirring, smells of ammonia.

$$K_2CrO_4,CrO_3 + 2NH_4HO = 2KNH_4CrO_4 + H_2O.$$

Other Analytical Reactions.—To a barium solution add a soluble carbonate (carbonate of ammonium (Am_2CO_3) will generally be rather more useful than others); a white precipitate of carbonate of barium ($BaCO_3$) results.——To more of the solution add an alkaline phosphate or arseniate (phosphate of sodium (Na_2HPO_4) is the most common of these chemically analogous salts, but phosphate of ammonium (Am_2HPO_4) or arseniate (Am_2HAsO_4) will subsequently have the preference); white phosphate of barium ($BaHPO_4$), insoluble in pure water, but slightly soluble in aqueous solutions of some salts, or arseniate of barium ($BaHAsO_4$), both soluble even in acetic and other weak acids, are precipitated.——To another portion add oxalate of ammonium ($Am_2C_2O_4$); white oxalate of barium (BaC_2O_4) is precipitated, soluble in the diluted mineral acids, and sparingly so in acetic acid.——The silico-fluoride of barium ($BaSiF_6$) is insoluble, and falls readily if an equal volume of spirit of wine be added to the solution under examination after the addition of hydrofluosilicic acid (H_2SiF_6).——Barium salts, moistened with hydrochloric acid, impart a greenish color to flame.

Mem.—Good practice will be found in writing out equations descriptive of each of the foregoing reactions.

QUESTIONS AND EXERCISES.

138. What is the quantivalence of barium?

139. Write down the formulæ of oxide, hydrate, chloride, nitrate, carbonate, and sulphate of barium; and state how these salts are prepared.

140. Describe the preparation of peroxide of hydrogen.

141. Which of the tests for barium are most characteristic? Give an equation of the reactions.

142. Name the antidote in cases of poisoning by soluble barium salts, and explain its action.

CALCIUM.

Symbol Ca. Atomic weight 40.

Calcium compounds form a large proportion of the crust of our earth. Carbonate of calcium is met with as chalk, marble, limestone, calc-spar, etc.; the sulphate, as gypsum or plaster of Paris (native sulphate of calcium—$CaSO_4,2H_2O$—deprived of water by heat), and alabaster; the silicate in many minerals; the fluoride of calcium as fluor-spar. The phosphate is also a common mineral. The element itself is only isolated with great difficulty. The atom of calcium is bivalent, Ca''.

REACTIONS HAVING SYNTHETICAL INTEREST.

Chloride of Calcium.

First Synthetical Reaction.—To some hydrochloric acid add carbonate of calcium (chalk, or, the purer form, white marble)

($CaCO_3$) until effervescence ceases, filter; solution of chloride of calcium ($CaCl_2$), the most common soluble salt of calcium, is formed.

$$\underset{\substack{\text{Carbonate of}\\ \text{calcium.}}}{CaCO_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} = \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\ \text{acid gas.}}}{CO_2}$$

This solution contains carbonic acid, and will give a precipitate of carbonate of calcium on the addition of lime-water. It may be obtained quite neutral by well boiling before filtering off the excess of marble. It is a serviceable test-liquid in analytical operations.

Solution of chloride of calcium evaporated to a syrupy consistence readily yields crystals ($CaCl_2,6H_2O$). These are extremely deliquescent. The solution, evaporated to dryness, and the white residue strongly heated, gives solid anhydrous chloride of calcium in a porous form. The resulting agglutinated lumps (*Calcii Chloridum*, U. S. P.) are much used for drying gases, and for freeing certain liquids from water. The salt is soluble in alcohol. One part of the crystals in ten of water constitutes a useful test-liquid, "Test-solution of Chloride of Calcium," U. S. P.

Mem.—The practical student has already met with solution of chloride of calcium as a by-product or secondary product in the preparation of carbonic acid gas.

Marble often contains ferrous carbonate ($FeCO_3$), which in the above process becomes converted into ferrous chloride, rendering the chloride of calcium impure:—

$$\underset{\substack{\text{Ferrous}\\ \text{carbonate.}}}{FeCO_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} = \underset{\substack{\text{Ferrous}\\ \text{chloride.}}}{FeCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\ \text{acid gas.}}}{CO_2}$$

If absolutely pure chloride of calcium be required, a few drops of the solution should be poured into a test-tube or test-glass, diluted with water, and examined for iron (by adding sulphydrate of ammonium, which gives a black precipitate with salts of iron), and, if the latter is present, hypochlorite of calcium (in the form of chlorinated lime) and slaked lime should be added to the remaining bulk of the liquid, and the whole boiled for a few minutes, whereby iron (as ferric hydrate) is thus precipitated; on filtering, a pure solution of chloride of calcium is obtained:—

$$\underset{\substack{\text{Ferrous}\\ \text{chloride.}}}{4FeCl_2} + \underset{\substack{\text{Hypochlorite}\\ \text{of calcium.}}}{Ca2ClO} + \underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{4CaH_2O_2} + \underset{\text{Water.}}{2H_2O}$$
$$= \underset{\substack{\text{Ferric}\\ \text{hydrate.}}}{2(Fe_26HO)} + \underset{\substack{\text{Chloride}\\ \text{of calcium.}}}{5CaCl_2}$$

This is the official process, and may be imitated on the small scale after adding a minute piece of iron to a fragment of the marble before disolving in acid.

The names, formulæ, and reactions of these compounds of iron will be best understood when that metal comes under treatment.

Oxide of Calcium (Quick Lime).

Second Synthetical Reaction.—Place a small piece of chalk in a strong grate-fire or furnace and heat until a trial fragment, chipped off from time to time and cooled, no longer effervesces on the addition of acid; caustic lime, CaO (*Calx*, U. S. P.), remains.

$$\underset{\text{Carbonate of calcium (chalk).}}{CaCO_3} = \underset{\text{Oxide of calcium (lime).}}{CaO} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Note.—Etymologically considered, this action is analytical (ἀναλύω, *analuo*, I resolve) and not synthetical (σύνθεσις, *sūnthesis*, a putting together); but conventionally it is synthetical, and not analytical; for in this, the usual sense, and the sense in which the words are used throughout this book, synthesis is the application of chemical action with the view of producing something, analysis the application of chemical action with the view of finding out the composition of a substance. In the etymological view of the matter, there is scarcely an operation performed either by the analyst or by the manufacturer but includes both analysis and synthesis—that is, includes interchange, or *metathesis.*

Lime-kilns.—On the large scale the above operation is carried on in what are termed *lime-kilns* (*Kiln*, Saxon, *cyln*, from *cylene*, a furnace).

Hydrate of Calcium (Slaked Lime).

Slaked Lime.—When cold, add to the lime about half its weight of water, and notice the evolution of steam and other evidence of strong action; the product is *slaked* lime or hydrate of calcium (Ca2HO), with whatever slight natural impurities the lime might contain. The slaking of hard or "stony" lime may be accelerated by using hot water.

$$\underset{\text{Lime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hydrate of calcium (slaked lime).}}{Ca2HO}$$

Lime-water.—Place the hydrate of calcium (washed with a little water to remove traces of soluble salts) in about a hundred times its weight of water; in a short time a saturated solution, known as *lime-water* (*Liquor Calcis*, U. S. P.), results. It contains about 0.15 per cent of slaked lime, or about 16 grains of hydrate of calcium (Ca2HO), equivalent to about 11 or 12 grains of lime (CaO), in one (Imperial) pint at 60° F., at higher temperatures less is dissolved. Sp. gr. 1.0015.

Strong Solution of Lime.—Slaked lime is much more soluble in aqueous solution of sugar than in pure water. The *Syrupus Calcis*, U. S. P., is such a solution, containing 5 parts of lime and 30 of sugar in 100 parts, by weight, of fluid.

Solutions of hydrate of calcium absorb carbonic acid gas on exposure to air, a semi-crystalline precipitate of carbonate being deposited. When the saccharated solution is heated, there is precipitated a compound consisting of three molecules of lime with one of sugar.

Carbonate of Calcium.

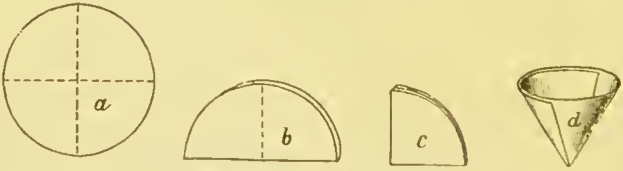
Third Synthetical Reaction.—To a solution of chloride of calcium add excess of carbonate of sodium, or about 5 parts of dry chloride to 13 of carbonate; a white precipitate of carbonate of calcium (*Calcii Carbonas Præcipitatus*, U. S. P.) ($CaCO_3$) results. If the solutions of the salts be made hot before admixture, and the whole set aside for a short time, the particles aggregate to a greater extent than when cold water is used, and the product is finely granular or slightly crystalline.

$$\underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Carbonate of calcium.}}{CaCO_3} + \underset{\text{Chloride of sodium.}}{2NaCl}$$

Collect and purify this *Precipitated Chalk* by pouring the mixture into a paper cone supported by a funnel, and, when the liquid has passed through the filter, pour water over the precipitate three or four times until the whole of the chloride of sodium is washed away. This operation is termed *washing a precipitate.* When dried by aid of a water-bath (p. 109) or other means, the precipitate is fit for use.

Filtering-paper, or *bibulous-paper* (from *bibo*, to drink), is simply good unsized paper made from the best white rags—white blotting-paper, in fact, of unusually good quality. Students' or analysts' filters, on which to collect precipitates, are circular pieces (*a*) of this paper, from three to six inches in diameter, twice folded (*b*, *c*), and then opened out so as to form a hollow cone (*d*). Square pieces are

Fig. 22.



Construction of Paper Filters.

rounded by scissors *after* twice folding. The cone is supported by a glass or earthenware funnel.

Filters should *always* be cut round so as to form a cone. If the square piece of paper is folded and used without being so cut or trimmed, an ugly angular filter results, from which it is difficult to wash all "mother-liquor" (the solution of chloride of sodium is the "mother-liquor" in the previous reaction). If a spirituous or other volatile liquor is being passed through such an angular filter, much of the liquid will also be wasted by evaporation from the unnecessarily large surface exposed.

Paper filters of large size are apt to break at the point of the cone. This may be prevented, and the rate of filtration be much accelerated, by supporting the paper cone in a cone of muslin.

Washing-bottle.—Precipitates are best washed by a fine jet of water directed on to the different parts of the filter. A common narrow-necked bottle of about half-pint capacity (Fig. 23) is fitted with a cork; two holes are bored through the cork, the one for a glass tube reaching to the bottom of the bottle within, and externally bent to a slightly acute angle, the other for a tube bent to a slightly obtuse angle, the inner arm terminating just within the bottle. The outer arms may be about 3 inches in length. The extremity of the outer arm continuous with the long tube should be previously drawn out to a fine capillary opening by holding the original tube, before cutting, in a flame, and, when soft, slowly pulling the halves away from each other until the heated portion is reduced to the thinness of a knitting-needle. The tube is now cut at the thin part by a file, and the sharp edges rounded off by placing in a flame for a second or two. The outer extremity of the shorter tube should also be made smooth in the flame. The apparatus being put together, and the bottle nearly filled with water, air, blown through the short tube by the lungs, forces water out in a fine stream at the capillary orifice.

Fig. 23.

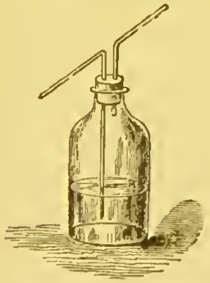
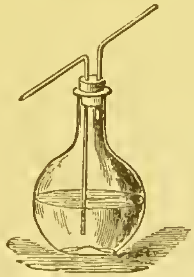


Fig. 24.

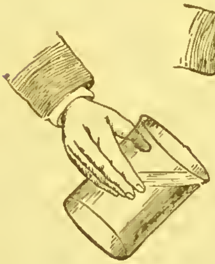


Washing-bottles.

For a *hot-water washing flask* (Fig. 24) the tubes and cork are fitted to a flask which may be heated. A strip of leather tied round the neck will protect the fingers.

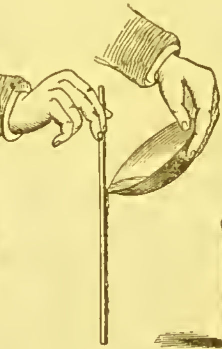
Decantation.—Precipitates may also be washed by allowing them to settle, pouring off the supernatant liquid (Fig. 25), agitating with water, again allowing to settle, and so on. This is washing by *decantation* (*de*, from, *canthus*, an edge). If a stream of liquid flowing from a basin or other vessel exhibits any tendency to run down the outer side of the vessel, it should be guided by a glass rod placed against the point whence the stream emerges (Fig. 26).

Fig. 25.



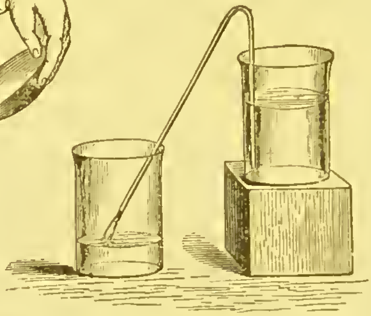
Decantation.

Fig. 26.



Decantation.

Fig. 27.



Siphon in action.

If the vessel be too large to handle with convenience, the wash-water may be drawn off by a *siphon*, as shown in miniature in Fig. 27. A siphon is a tube of glass, metal, gutta-percha, or India-rubber bent into the form of a V or U, filled with water, and inverted; one end immersed in the wash-water, and the other allowed to hang over the side of the vessel. So long as the outer orifice of the instrument is below the level of any liquid in the vessel, so long will that liquid flow from within outwards.*

Prepared carbonate of calcium (*Creta Præparata*, U. S. P.) is merely washed chalk or *whiting*, only that in Pharmacy fashion demands that the chalk be in little conical lumps, about the size of thimbles, instead of the larger rolls characteristic of "whiting." Wet whiting pushed, portion by portion, through a funnel, and each separately dried, gives the conventional *Creta Præparata*. Its powder is amorphous.

Testa Præparata is powdered oyster-shell, similarly treated. It is an inferior kind of prepared chalk.

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* *The nature of the action of a siphon* is simple. The column of water in the outer limb is longer, and therefore heavier than the column of similar area in the inner limb. (The length of the inner limb must be reckoned from the surface of the liquid, the portion below the surface playing no part in the operation.) Being heavier, it naturally falls by gravitation, the liquor in the shorter limb instantly following, because pressed upwards by the air. The air, be it observed, exerts a similar amount of pressure on the liquid in the outer limb: in short, atmospheric pressure causes the retention of liquid in the instrument, while gravitation determines the direction of the flow.

Phosphate of Calcium.

Fourth Synthetical Reaction.—Digest bone-ash (bones burnt in an open crucible with free access of air till all animal and carbonaceous matter has been removed—impure phosphate of calcium (*Os Ustum*, B. P.)) with nearly twice its weight of hydrochloric acid (diluted with three or four times its bulk of water), in a test-tube or larger vessel; the phosphate is dissolved.

$$\underset{\substack{\text{Phosphate of}\\ \text{calcium (impure).}}}{Ca_32PO_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} = \underset{\substack{\text{Acid phosphate}\\ \text{of calcium.}}}{CaH_42PO_4} + \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{2CaCl_2}$$

Dilute with water, filter, boil, and when cold add excess of solution of ammonia; the phosphate of calcium, now pure (*Calcii Phosphas Præcipitatus*, U. S. P.), is reprecipitated as a light white amorphous powder. After well washing, the precipitate should be dried over a *water-bath* (see below), or at a temperature not exceeding 212°, to prevent undue aggregation of the particles.

$$\underset{\substack{\text{Acid phosphate}\\ \text{of calcium.}}}{CaH_42PO_4} + \underset{\substack{\text{Chloride}\\ \text{of calcium.}}}{2CaCl_2} + \underset{\text{Ammonia.}}{4AmHO} = \underset{\substack{\text{Phosphate}\\ \text{of calcium}\\ \text{(pure).}}}{Ca_32PO_4} + \underset{\substack{\text{Chloride of}\\ \text{ammonium.}}}{4AmCl} + \underset{\text{Water.}}{4H_2O}$$

Bone-ash or bone-earth contains small quantities of carbonate and sulphide of calcium. These are decomposed in the above process by the acid, chloride of calcium being formed; on boiling the mixture, carbonic acid gas and sulphuretted hydrogen gas are evolved. Any carbonaceous or siliceous matter, etc. is removed by filtration. In bones the phosphate of calcium is always accompanied by a small quantity of an allied substance, phosphate of magnesium; a trace of fluoride of calcium (CaF_2) is also present.

A *Water-bath* for the evaporation of liquids or for drying moist solids at temperatures below 212° F. is an iron, tin, or earthenware pan, the mouth of which can be narrowed by iron or tin diaphragms of various sizes, and having orifices adapted to the diameters of evaporating dishes or plates. In the British Pharmacopœia, "when a *water-bath* is directed to be used, it is to be understood that this term refers to an apparatus by means of which water or its vapor, at a temperature not exceeding 212°, is applied to the outer surface of a vessel containing the substance to be heated, which substance may thus be subjected to a heat near to, but necessarily below, that of 212°. In the *steam-bath* the vapor of water at a temperature above 212°, but not exceeding 230°, is similarly applied." Evaporation *in vacuo* is performed by simply placing the vessel of liquid over or by the side of a small reservoir of strong sulphuric acid, or other absorbent of moisture, on the plate of an air-pump, covering with a capacious glass hood or "receiver," and exhausting.

Bone-black, or *Animal Charcoal* (*Carbo Animalis*, U. S. P.), is the residue obtained on subjecting dried bones to a red heat without access of air. The operation may be imitated by heating a few fragments of bone in a covered porcelain crucible in a fume-chamber until smoke and vapor cease to be evolved. Purified Animal Charcoal (*Carbo Animalis Purificatus*, U. S. P.) is obtained by digesting animal charcoal (2 parts) in hydrochloric acid (3 parts) and water (30 parts) in a warm place for a day or so, filtering, thoroughly washing, drying over a water-bath, and igniting the product in a closely covered crucible. The reaction is the same as that just described; that is to say, the acid removes the phosphate of calcium from the carbon of animal charcoal by forming soluble acid phosphate and chloride of calcium.

Wood Charcoal (*Carbo Ligni*, U. S. P.) is wood similarly ignited without access of air.

Decolorizing Power of Animal Charcoal.—Animal charcoal, in small fragments, is the material employed in decolorizing solutions of common brown sugar with the view of producing white lump sugar. Its power and the nearly equal power of an equivalent quantity of the purified variety may be demonstrated on solution of litmus or logwood.

Syrupus Calcii Lacto-phosphatis, U. S. P., is a flavored solution of precipitated phosphate of calcium in lactic acid.

Phosphate of Sodium.—Phosphate of calcium is converted into phosphate of sodium (*Sodii Phosphas*, U. S. P.) (Na_2HPO_4, $12H_2O$) as follows: Mix, in a mortar, 3 ounces of ground bone-earth with one fluidounce of sulphuric acid; set aside for twenty-four hours to promote reaction; mix in about 3 ounces of water, and put in a warm place for two days, a little water being added to make up for that lost by evaporation; stir in another 3 ounces of water, warm the whole for a short time, filter, and wash the residual sulphate of calcium on the filter to remove adhering acid phosphate of calcium; concentrate the *filtrate* (the liquid portion), which is a solution of acid phosphate of calcium, to about 3 ounces, filter again, if necessary, add solution of (about 4½ ounces of crystals of) carbonate of sodium to the hot filtrate until a precipitate (a phosphate of calcium, $CaHPO_4$) ceases to form, and the fluid is faintly alkaline; filter, evaporate, and set aside to crystallize.

Phosphate of sodium occurs "in transparent colorless rhombic prisms, terminated by four converging planes, efflorescent, tasting like common salt." One part to ten of water constitutes "Solution of Phosphate of Soda," B. P. This is an official as well as the ordinary process. The following equations show the two decompositions which occur during the operation:—

Ca_32PO_4	+	$2H_2SO_4$	=	CaH_42PO_4	+	$2CaSO_4$
Phosphate of calcium.		Sulphuric acid.		Acid phosphate of calcium.		Sulphate of calcium.
CaH_42PO_4	+	Na_2CO_3	=	Na_2HPO_4	+	H_2O
Acid phosphate of calcium.		Carbonate of sodium.		Phosphate of sodium.		Water.
	+	CO_2	+	$CaHPO_4$		
		Carbonic acid gas.		Phosphate of calcium.		

Ordinary phosphate of sodium ($Na_2HPO_4,12H_2O$) effloresces rapidly in the air until nearly half its water has escaped, when it has a permanent composition represented by the formula $Na_2HPO_4,7H_2O$. Phosphate of sodium has an alkaline reaction; neutralization by acid results in the removal of half its sodium and formation of the salt NaH_2PO_4,H_2O.

Hypochlorite of Calcium.

Fifth Synthetical Reaction.—Pass chlorine, generated as already described, into damp slaked lime contained in a piece of wide tubing, open at the opposite end to that in which the delivery-tube is fixed. (A test-tube, the bottom of which has been accidentally broken, is very convenient for such operations.) The product is ordinary *bleaching-powder*, a compound of hypochlorite and chloride of calcium, commonly called *chloride of lime* (*Calx Chlorata*, U. S. P.).

MnO_2	+	$4HCl$	=	$MnCl_2$	+	$2H_2O$	+	Cl_2
Black oxide of manganese.		Hydrochloric acid.		Chloride of manganese.		Water.		Chlorine.
$2CaH_2O_2$	+	$2Cl_2$	=	$2H_2O$	+	$CaCl_2O_2$	,	$CaCl_2$
Hydrate of calcium.		Chlorine.		Water.		Hypochlorite of calcium.		Chloride of calcium.

Chlorinated lime, exposed to air and moisture, as in disinfecting the air of sick-rooms, slowly yields hypochlorous acid ($HClO$). Free hypochlorous acid soon breaks up into water, chloric acid ($HClO_3$), and free chlorine. Chloric acid is also unstable, decomposing into oxygen, water, chlorine, and perchloric acid ($HClO_4$). The small quantity of hypochlorous acid diffused through an apartment when bleaching-powder is exposed thus, yields fourteen-fifteenths of its chlorine in the form of chlorine gas—one of the most efficient of known disinfectants.

Constitution of Bleaching-powder.—Treated with alcohol, bleaching-powder does not yield its chloride of calcium to the solvent, hence the powder is not a mere mixture of chloride and hypochlorite of calcium: water, also, does not dissolve out first one salt, and then the other, but both together, in the molecular proportions of the above formula. On the other hand, when the aqueous solution is cooled, or evaporated *in vacuo*, crystals are obtained which Kingzett has shown to be nearly pure hypochlorite of calcium, the solution containing chloride of calcium. While the former fact indicates that the powder is a compound, and not a mere mixture, the latter indicates that it is a feeble compound; an adhesion of molecules of hypochlorite and chloride, as shown in the equation, rather than any more intimate or closer combination of atoms. If it be regarded as a single rather than a double salt, then the following formula may be employed, $Ca\left\{\begin{matrix}Cl\\ClO\end{matrix}\right.$.

Bleaching-liquor.—Digest chlorinated lime in water, in which the bleaching compound is soluble, filter from the undissolved lime, and test the bleaching powers of the clear liquid by adding a few drops to a decoction of logwood slightly acidulated. One pound of this bleaching-powder, shaken several times during three hours with 1 gallon of water, forms Solution of Chlorinated Lime (*Liquor Calcis Chloratæ*, B. P.).

Sixth Synthetical Reaction.—Heat a mixture of 10 parts of powdered lime and 9 of sulphur in a crucible having a luted cover for an hour. The product, when cold, rubbed to powder, constitutes Sulphurated Lime (*Calx Sulphurata*, U. S. P.). It should contain not less than 36 per cent. of sulphide of calcium (CaS); the remainder is sulphate, with, probably, sulphite and hyposulphite of calcium.

Gummate of Calcium.

Gummate of Calcium is the only official calcium salt that remains to be noticed. This compound is, in short, *arabin*, the ordinary Gum Acacia, or Gum Arabic (*Acacia*, U. S. P.), a substance too well known to need description. A solution of gum arabic in water (*Mucilago Acaciæ*, U. S. P.) yields a white precipitate of oxalate of calcium on the addition of solution of oxalate of ammonium. Or a piece of gum burnt to an ash in a porcelain crucible yields a calcareous residue, which, dissolved in dilute acids, affords characteristic reactions with any of the following analytical reagents for calcium. In some specimens of gum arabic a portion of the calcium is displaced by an equivalent quantity of potassium or magnesium. The gummic radical may be precipitated as opaque gelatinous gummate of lead by the addition of solution of oxyacetate of lead (*Liquor Plumbi Subacetatis*, U. S. P.) to an aqueous solution of gum. These statements may be experimentally verified by the practical student.

Tragacanth (*Tragacantha*, U. S. P.) is a mixture of soluble arabinoid gum and a variety of calcium gum insoluble in water, termed *bassorin*. With water a gelatinous mucilage is formed (*Mucilago Tragacanthæ*, U. S. P., contains 6 parts of tragacanth, 18 of glycerin, and 76 of water).

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Add sulphuric acid, very highly diluted, to a calcium solution contained in a test-tube or small test-glass; sulphate of calcium ($CaSO_4,2H_2O$) is formed, but is *not* precipitated, it being, unlike sulphate of barium, slightly soluble in water.

Solution of Sulphate of Calcium.—A quarter of an ounce of that (dried) form of sulphate of calcium known as plaster of Paris ($CaSO_4$) digested in one pint of water for a short time, with occasional shaking, and the mixture filtered, yields the official test-liquid termed "Solution of Sulphate of Lime," B. P. About 400 parts of the solution contain 1 of calcium.

Second Analytical Reaction.—Add yellow chromate of potassium (K_2CrO_4), or other neutral chromate ($KAmCrO_4$), to a calcium solution slightly acidified with acetic acid; chromate of calcium ($CaCrO_4$) is probably formed, but it is *not* precipitated. Barium is precipitated by the chromic radical.

These two negative reactions are most valuable in analysis, as every precipitant of calcium is also a precipitant of barium; but the above two reagents are precipitants of barium only. Hence calcium, which when alone can be readily detected by the following reactions, cannot by any reaction be detected in the presence of barium. But by the sulphuric or chromic test barium is easily removed, and then either of the following reagents will throw down the calcium.

Other Analytical Reactions.—Add carbonate of ammonium, phosphate of sodium, arseniate of ammonium, and oxalate of ammonium to calcium solutions as described under the analytical reactions of barium, and write out descriptive equations. The precipitates correspond in appearance to those of barium;

their constitution is also similar, hence their correct formulæ can easily be deduced. Of these precipitants oxalate of ammonium is that most commonly used as a reagent for calcium salts, barium being absent. The oxalate of calcium is insoluble in acetic, but soluble in hydrochloric or nitric acid.——Calcium compounds impart a reddish color to the flame.

QUESTIONS AND EXERCISES.

143. Enumerate some of the common neutral compounds of calcium.

144. Explain, by an equation, the action of hydrochloric acid on marble. What official compounds result?

145. Why is chloride of calcium used as a desiccator for gases?

146. How would you purify Chloride of Calcium which has been made from ferruginous marble? Give diagrams.

147. Write a few lines on the chemistry of the lime-kiln.

148. In what sense is the conversion of chalk into lime an analytical action?

149. What occurs when lime is "slaked"?

150. To what extent is lime soluble in water? to what in syrup?

151. Describe the preparation of the official Precipitate of Carbonate of Calcium; in what does it differ from Prepared Chalk?

152. In what does filtering-paper differ from other kinds of paper?

153. Explain the construction of "a washing-bottle" for cleansing precipitates by water.

154. Describe *decantation.*

155. Describe the construction and manner of employment of a siphon.

156. Explain the mode of action of a siphon.

157. What is the difference between Bone, Bone-earth, and Precipitated Phosphate of Calcium?

158. How is "Bone-earth" purified for use in medicine?

159. Explain the action of hydrochloric acid on Animal Charcoal in the conversion of *Carbo Animalis* into *Carbo Animalis Purificatus.*

160. What is the chemical difference between *Carbo Animalis* and *Carbo Ligni?*

161. Give equations showing the conversion of Phosphate of Calcium into Phosphate of Sodium.

162. Write a short article on the manufacture, composition, and uses of "bleaching-powder."

163. How may calcium be detected in Gum Arabic?

164. State the chemical nature of Tragacanth.

165. To what extent is sulphate of calcium soluble in water?

166. Can calcium be precipitated from an aqueous solution containing barium?

167. Barium being absent, what reagents may be used for the detection of calcium? Which is the chief test?

MAGNESIUM.

Symbol Mg. Atomic weight 24.

Source.—Magnesium is abundant in nature in the form of magnesian or mountain limestone, or *dolomite*, a double carbonate of magnesium and calcium in common use as a building-stone (*e. g.*, the Houses of Parliament and the School of Mines in London), and *magnesite*, a tolerably pure carbonate of magnesium, though too "stony" for direct use in medicine, even if very finely powdered. Chloride of magnesium and sulphate of magnesium (Epsom salt) also occur in sea-water and in the water of many springs. A monohydrous sulphate ($MgSO_4,H_2O$) termed *kieserit* occurs near Stassfurt in Prussia. Metallic magnesium may be obtained from the chloride by the action of sodium. It burns readily in the air, emitting a dazzling light, due to the white heat to which the resulting particles of magnesia (MgO) are exposed. The chloride employed as a source of the metal is obtained by dissolving the carbonate in hydrochloric acid, adding some chloride of ammonium, evaporating to dryness, heating the residue in a flask (on the small scale a large test-tube or Florence flask) until the chloride of ammonium is all volatilized and the chloride of magnesium remains as a clear fused liquid. The latter is poured on to a clean earthenware slab. The chloride of ammonium prevents reaction between chloride of magnesium and water in the last stages of the operation and consequent formation of oxide (or oxychloride) of magnesium and hydrochloric acid gas.

Quantivalence.—The atom of magnesium is bivalent, Mg''.

REACTIONS HAVING SYNTHETICAL INTEREST.

Sulphate of Magnesium.

First Synthetical Reaction.—To a few drops of sulphuric acid and a little water in a test-tube, made hot (or to larger quantities in larger vessels), add powdered native carbonate of magnesium, *magnesite*, $MgCO_3$, until effervescence ceases, subsequently boiling to aid in the expulsion of the carbonic acid gas. The filtered liquid is a solution of sulphate of magnesium ($MgSO_4$), crystals of which, *Epsom salt* ($MgSO_4,7H_2O$) (*Magnesii Sulphas*, U. S. P.), may be obtained on evaporating most of the water and setting the concentrated solution aside to cool. This is an ordinary manufacturing process. Instead of magnesite, *dolomite*, the common magnesian limestone (carbonate of magnesium and calcium, $CaCO_3,MgCO_3$), may be employed, any iron being removed by evaporating the solution (filtered from the sulphate of calcium produced) to dryness, gently igniting to decompose sulphate of iron, dissolving in water, filtering from oxide of iron, and crystallizing. (If neither mineral be at hand, the practical student may use a little of the ordinary manufactured carbonate of pharmacy, for the chemical action is almost identical, and it is the chemistry and not, just now, the commercial economy of the matter that he is studying. The manufacturer must, of course, commence with one of the above mineral carbonates furnished by nature, from that make his sulphate, and from the latter, as will be seen directly, make the pure pulverulent carbonate of pharmacy.)

$$\underset{\substack{\text{Carbonate of}\\\text{magnesium.}}}{MgCO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate of}\\\text{magnesium.}}}{MgSO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

Sulphate of magnesium readily crystallizes in large, colorless, transparent, rhombic prisms; but, from concentrated solutions, the crystals are deposited in short thin needles, a form more convenient for manipulation, solution, and general use in medicine.

Iron may be detected in sulphate of magnesium by adding the common alkaline solution of chlorinated lime or chlorinated soda to some aqueous solution of the salt; brown hydrate of iron (Fe_26HO) being precipitated. Sulphydrate ammonium will also give a black precipitate if iron be present.

Carbonates of Magnesium.

Second Synthetical Reaction.—To solution of sulphate of magnesium add solution of carbonate of sodium, and boil; the resulting precipitate is *light* carbonate of magnesium (*Magnesiæ Carbonas Levis*, B. P.; *Magnesii Carbonas*, U. S. P.), a white, partly amorphous, partly minutely crystalline mixture of carbonate and hydrate of magnesium ($3MgCO_3,Mg2HO,4H_2O$, B. P.; $4MgCO_3,Mg2HO,5H_2O$, U. S. P.). A denser, slightly granular precipitate of similar chemical composition (*Magnesiæ Carbonas*, B. P.) is obtained on mixing strong solutions of the above salts, evaporating to dryness, then removing the sulphate of sodium by digesting the residue in hot water, filtering, washing, and drying the precipitate.

$$\underset{\substack{\text{Sulphate of}\\\text{magnesium.}}}{4MgSO_4} + \underset{\substack{\text{Carbonate of}\\\text{sodium.}}}{4Na_2CO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Official carbonate of}\\\text{magnesium.}}}{3MgCO_3,Mg2HO}$$

$$+ \underset{\substack{\text{Sulphate of}\\\text{sodium.}}}{4Na_2SO_4} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

The official (B. P.) proportions for the light carbonate are 10 of sulphate of magnesium and 12 of crystals of carbonate of sodium, each dissolved in 80 of cold water, the solutions mixed, boiled for 15 minutes, the precipitate collected on a filter, well washed, drained, and dried over a water-bath. The heavier carbonate is made with the same proportions of salts, each dissolved in 20 instead of 80 of water, the mixture evaporated quite to dryness, and the residue washed by decantation or filtration until all sulphate of sodium is removed (shown by a white precipitate—sulphate of barium—ceasing to form on the addition of solution of chloride or nitrate of barium to a little of the filtrate).

Another (Pattinson's) Process.—Considerable quantities of carbonate of magnesium are now prepared by treating dolomite (see p. 115) with carbonic acid under pressure. Of the two carbonates the magnesian is dissolved first, and is precipitated from the clear liquid by the heat of a current of steam. (See next reaction.)

Third Synthetical Reaction.—Pass carbonic acid gas, generated as described on page 71, into a mixture of water and carbonate of magnesium contained in a test-tube. After some time, separate undissolved carbonate by filtration; the filtrate contains carbonate of magnesium dissolved by carbonic acid. When of a strength of about 13 grains in one ounce, such a solution constitutes "*Fluid Magnesia*" (*Liquor Magnesiæ Carbonatis*, B. P.). This strength of about 3 per cent. at about 55° F. is reduced to 2½ per cent. at 70° and to about 2 per cent. at 80° F.

Officially, 1 pint is directed to be made from freshly prepared carbonate. The latter is obtained by adding a hot solution of 2 ounces of sulphate of magnesium in half a pint of water to one of 2½ ounces of crystals of carbonate of sodium in another half pint of water, boiling the mixture for a short time (to complete decomposition), filtering, thoroughly washing the precipitate, placing the latter in 1 pint of distilled water, and transmitting carbonate acid gas through the liquid (say, at the rate of three or four bubbles per second) for an hour or two, then leaving the solution in contact with the gas under slight pressure for twenty-four hours, and, finally, filtering from undissolved carbonate, and, after passing in a little more gas, keeping in a well-corked bottle. Slight pressure is best created by placing the carbonate and water in a bottle fitted with a cork and tubes as for a wash-bottle (p. 96 or 107), conveying the gas by the tube which reaches to the bottom, and allowing excess of gas to flow out by the upper tube, the external end of which is continued to the bottom of a common phial containing about an inch of mercury. The phial should be loosely plugged with cotton-wool, to prevent loss of metal by spurting during the flow of the gas through it. (Each inch in depth of mercury through which the gas escapes corresponds to about half a pound pressure on every square inch of surface within the apparatus.)

Heat a portion of the solution; true carbonate of magnesium containing combined water ($MgCO_3,3H_2O$) is precipitated. The water in this compound is probably in the state of water of crystallization, for a salt having the same composition is deposited in crystals by the spontaneous evaporation of the solution of carbonate of magnesium. The official "carbonate" ($3MgCO_3,Mg2HO,4H_2O$) is another of these very common *hydrous* compounds.

Exposed to cold, the solution of "fluid magnesia" sometimes affords large thick crystals ($MgCO_3,5H_2O$), which, in contact with the air, lose water, become opaque, and then have the composition of those deposited by evaporation ($MgCO_3,3H_2O$).

Oxide of Magnesium (Magnesia).

Fourth Synthetical Reaction.—Heat light dry carbonate of magnesium in a porcelain crucible over a lamp (or in a larger earthen crucible in a furnace) till it ceases to effervesce on adding, to a small portion, water and acid; the residue is light magnesia (MgO) (*Magnesia Levis*, B. P.; *Magnesia*, U. S. P.). The same operation on the heavy carbonate yields heavy magnesia (MgO) (*Magnesia*, B. P.; *Magnesia Ponderosa*, U. S. P.). Both are sometimes spoken of as "calcined magnesia." A given weight of the official light magnesia occupies three and a half times the bulk of the weight of heavy magnesia.

$$\underset{\substack{\text{Official carbonate of}\\\text{magnesium.}}}{3MgCO_3,Mg2HO} = \underset{\substack{\text{Oxide of}\\\text{magnesium.}}}{4MgO} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

A trace only of magnesia is dissolved by pure water. Moisten a grain or two of magnesia with water, and place the paste on a piece of red litmus-paper; the wet spot, after a time, becomes blue, showing that the magnesia is slightly soluble.

"*Effervescing Citrate of Magnesia*," so called, is generally a mixture of bicarbonate of sodium, citric acid, tartaric acid, sugar, either carbonate or sulphate of magnesium, or both, and flavoring essences. True citrate of magnesium is easily made by heating together calcined magnesia and citric acid; it is frequently prescribed in France in doses of two ounces.

The official "Granulated Citrate of Magnesium" (*Magnesii Citras Granulatus*, U. S. P.) is made as follows: Mix 11 parts of carbonate of magnesium intimately with 33 of citric acid, and enough distilled water to make a thick paste; dry this at a temperature not exceeding 30° C (86° F.), and reduce it to a fine powder. Then mix it intimately with 8 of sugar (No. 60 powder), 37 of bicarbonate of sodium, and 15 of citric acid previously reduced to a very fine powder. Dampen the mass with a sufficient quantity of alcohol, and rub it through a No. 20 tinned-iron sieve, to form a coarse, granular powder. Lastly, dry it in a moderately warm place.

The official Effervescing "Solution of Citrate of Magnesium" (*Liquor Magnesii Citratis*, U. S. P.) is made by dissolving carbonate of magnesium in slight excess of solution of citric acid, adding syrup of citric acid, placing the diluted liquid in an aërated-water bottle, dropping in crystals of bicarbonate of potassium, corking, "wiring," and shaking till the crystals are dissolved.

The formula of citrate of magnesium deposited from solution is $Mg_32C_6H_5O_7,14H_2O$.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Add solution of hydrate or carbonate of ammonium to a magnesian solution (sulphate, for example) and warm the mixture in a test-tube; the precipitation of part only of the magnesium as hydrate ($Mg2HO$) or carbonate ($MgCO_3$) occurs. Add now to a small portion of the mixture of precipitate and liquid a considerable excess of solution of chloride of ammonium; the precipitate is dissolved.

This is an important reaction, especially as regards carbonate of magnesium, the presence of chloride of ammonium enabling the analyst to throw out from a solution barium and calcium by an alkaline carbonate, magnesium being retained. The cause of this retention is found in the tendency of magnesium to form soluble double salts with potassium, sodium, or ammonium. In analysis, the chloride of ammonium should be added before the carbonate, as it is easier to prevent precipitation than to redissolve a precipitate once formed.

Second Analytical Reaction.—To some of the solution resulting from the last reaction, add solution of phosphate of sodium or ammonium; phosphate of magnesium and ammonium ($MgNH_4PO_4$) is precipitated.——*3d.* To another portion add arseniate of ammonium; arseniate of magnesium and ammonium ($MgNH_4AsO_4$) is precipitated.

Note.—Barium and calcium are also precipitated by alkaline phosphates and arseniates. The other precipitants of magnesium are also precipitants of barium and calcium. In other words, there is no *direct* test for magnesium. Hence the analyst always removes any barium or calcium by an alkaline carbonate, as above indicated; the phosphate of sodium, or arseniate or phosphate of ammonium, then becomes a very delicate test of the presence of magnesium. In speaking of magnesium tests, the absence of barium and calcium salts is to be understood.

QUESTIONS AND EXERCISES.

168. Name the natural sources of the various salts of magnesium.

169. Give a process for the preparation of Epsom salt.

170. Draw diagrams illustrative of the formation of sulphate of magnesium from *magnesite* and from *dolomite.*

171. Show by an equation the process for the preparation of the official Carbonate of Magnesium.

172. What circumstances determine the two different states of aggregation of the *Magnesiæ Carbonas* and *Magnesiæ Carbonas Levis?*

173. What are the relations of *Magnesia* and *Magnesia Levis* to the British official Carbonates of Magnesium?

174. How much denser is the one than the other?

175. Is magnesia soluble in water?

176. How is "Fluid Magnesia" prepared?

177. Mention the effects of heat and cold on "Fluid Magnesia."

178. How much magnesia (MgO) can be obtained from 100 grains of Epsom salt?

179. Calculate the amount of official Carbonate of Magnesium which will yield 100 grains of magnesia.

180. Can magnesium be detected in presence of barium and calcium?

181. Describe the analysis of an aqueous liquid containing salts of barium, calcium, and magnesium.

182. How may magnesium be precipitated from solutions containing ammoniacal salts?

Quantivalence.

On reviewing the foregoing statements regarding compounds of the three univalent radicals, potassium, sodium, and ammonium, and the three bivalent elements, barium, calcium, and magnesium, the doctrine of quantivalence will be more clearly understood, and its usefulness more apparent. Quantivalence, or the value of atoms, is, in short, in chemistry, closely allied to value in commercial barter. A number of articles, differing much in weight, appearance, and general characters, may be of equal money value: and if these be regarded, for convenience, as having a sort of unit of value, others worth double as much might be termed bivalent, three times as much trivalent, and so on. In like manner, chemical radicals, no matter whether elementary, like potassium (K), iodine (I), or sulphur (S), or compound, like those of nitrates (NO_3), sulphates (SO_4), or acetates ($C_2H_3O_2$), have a given chemical value in relation to each other, and are exchangeable for, and will unite with, each other to an extent determined by that value.

Most chemical salts apparently, though probably not really, have two parts, a basylous and acidulous, the one quantivalently balancing the other. The formulæ of the chief of these radicals and their quantivalence are given on the following page. Examples of formulæ of salts containing univalent, bivalent, and trivalent radicals are also appended.

QUANTIVALENCE OF COMMON RADICALS.

Univalent Radicals, or *Monads*.		Bivalent Radicals, or *Dyads*.		Trivalent Radicals, or *Triads*.	
Acidulous.	Basylous.	Acidulous.	Basylous.	Acidulous.	Basylous.
H	H	O	Ca	PO_4	As
Cl	K	SO_4	Mg	BO_3	Sb
I	Na	CO_3	Zn	$C_6H_5O_7$	Bi
HO	NH_4	C_2O_4	Cu	AsO_3	Fe^{iii}(ic)
NO_3	Ag	$C_4H_4O_6$	Hg(ic)	AsO_4	or
$C_2H_3O_2$	Hg(ous)	S	Fe(ous)	$C_4H_3O_5$	Fe^{vi}_2(ic)

Note.—The hydrogen (H) in the basylous parts of salts has entirely different functions from the hydrogen (H) in the acidulous part. The latter gives compounds commonly termed *hydrides* (*e. g.*, AsH_3); in the former the element is the basylous radical of acids (*e. g.*, HCl, H_2SO_4). In compound radicals (*e. g.*, $C_2H_3O_2$ or NH_4) the properties of hydrogen are no longer apparent; the chemical force resident in the atoms of such radicals seems to be mainly exerted in binding those atoms together.

Examples of Formulæ of Salts containing Univalent, Bivalent, and Trivalent Radicals.

The reader will find instructive practice in writing twenty or thirty imaginary formulæ of salts by placing in juxtaposition acidulous and basylous radicals, as in the following examples. Just as in a pair of scales a 2-lb. weight must be balanced by two 1-lb. weights, or a 4-lb. weight by two 2-lb. weights, or by one 3-lb. and one 1-lb. weight, so a bivalent radical unites with a bivalent radical or with two univalent radicals, a quadrivalent radical with two bivalent radicals, or with one trivalent and one univalent radical, and so on.

(R = any basylous Radical.) (*R* = any acidulous Radical.)

General formula.	*Examples.*
$\mathrm{R}'R'$	KI, NaCl, $NH_4C_2H_3O_2$, $AgNO_3$.
$\mathrm{R}''R'_2$	$CaCl_2$, $Zn2C_2H_3O_2$, $Pb2NO_3(BaNO_3C_2H_3O_2)$.
$\mathrm{R}'''R'_3$	$Bi3NO_3$, AsH_3, $SbCl_3$.
R'_2R'' . .	K_2CO_3, Na_2SO_4, $H_2C_4H_4O_6$.
$\mathrm{R}'\mathrm{R}'R''$ . .	$KHCO_3$, $NaHSO_4$ $KNaC_4H_4O_6$.
R'_3R''' . .	Am_3PO_4, $K_3C_6H_5O_7$, H_3AsO_3.
$\mathrm{R}'_2\mathrm{R}'R'''$.	Na_2HPO_4, Na_2HAsO_4.
$\mathrm{R}''R''$	$CaCO_3$, MgO, $CuSO_4$, HgO, $FeSO_4$.
$\mathrm{R}''_3R'''_2$	Ca_32PO_4, $Ca_32C_6H_5O_7$.
$\mathrm{R}''\mathrm{R}'R'''$ . . .	$MgAmPO_4$, $CuHAsO_3$.
$\mathrm{R}'''R''R'$ . . .	$BiONO_3$.
$\mathrm{R}'''_2R''_2R''$. . .	$Bi_2O_2CO_3$.
$\mathrm{R}'''_2R''_3$	As_2O_3, Sb_2O_3, Fe_2O_3, Fe_23SO_4.
$\mathrm{R}'''R'''$	$BiC_6H_5O_7$.
$\mathrm{R}'''_2R'_6$	Fe_2Cl_6, Fe_26NO_3, $Fe_26C_2H_3O_2$.

Quadrivalent Radicals or *Tetrads*, Quinquivalent Radicals or *Pentads*, and Sexivalent Radicals or *Hexads*, are known.

EXERCISE.

183. Write an exposition of the doctrine of Quantivalence within the limits of a sheet of note paper.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION* OF A SALT OF **ONE** OF THE METALS, BARIUM, CALCIUM, MAGNESIUM.

Add yellow chromate of potassium to a portion of the solution to be examined; a precipitate indicates barium.

If no barium is present, add chloride and carbonate of ammonium, and boil; a precipitate indicates calcium.

If barium and calcium are proved to be absent, add chloride of ammonium, ammonia, and then either phosphate of sodium or arseniate of ammonium; a white granular precipitate indicates magnesium.

Ammonia is here added to yield the necessary elements to ammonio-magnesian phosphate or ammonio-magnesian arseniate, both of which are highly characteristic precipitates; and chloride of ammonium is added to prevent a mere partial precipitate of the magnesium by the ammonia.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF **ONE, TWO, OR ALL THREE** OF THE METALS, BARIUM, CALCIUM, MAGNESIUM.

Add chromate of potassium to the solution; barium, if present, is precipitated. Filter, if necessary, and add to the *filtrate* (that is, the liquid which has run through the filter) chloride, hydrate, and carbonate of ammonium, and boil; calcium, if present, is precipitated. Filter, if requisite, and add phosphate of sodium; magnesium, if present, is precipitated.

Note.—Red chromate of potassium must not be used in these operations, or a portion of the barium will remain in the liquid and be thrown down with, or in place of, the carbonate of calcium (*vide* p. 102). The yellow chromate must not contain carbonate of potassium, or calcium will be precipitated with, or in place of, barium.

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* In preparing such solutions for analysis, salts should be selected which do not decompose each other. Chlorides will serve in most cases, but nitrates and acetates are still more convenient.

The absence of carbonate is proved by the non-occurrence of effervescence on the addition of hydrochloric acid to a little of the solution of the chromate, previously made hot in a test-tube. If the yellow chromate has been prepared by adding excess of ammonia to solution of red chromate of potassium, its addition to the liquid to be analyzed must be preceded by that of solution of chloride of ammonium, the precipitation of a portion of the magnesium (by the free ammonia in the yellow chromate) is thus prevented, for chloride of ammonium solution is a good solvent of hydrate (and carbonate) of magnesium, as already stated on page 119.

Note 1.—The analysis of solutions containing the foregoing metals is commenced by the addition of chloride of ammonium (AmCl) and ammonia (AmHO), simply as a precautionary measure, the former compound preventing partial precipitation of magnesium, the latter neutralizing acids. The carbonate of ammonium (Am_2CO_3) is the important group reagent—the precipitant of barium and calcium.

Note 2.—In the following, and in subsequent charts of analytical processes, the leading precipitants will be found to be ammonium salts. These, being volatile, can be got rid of towards the end of the operations, and thus the detection of potassium and sodium be in no way prevented—an advantage which could not be had if such salts as chromate of potassium or phosphate of sodium were the group-precipitants employed.

Note 3.—Acetic, and not hydrochloric or nitric, acid is used in dissolving the barium and calcium carbonates, because chromate of barium, on the precipitation of which the detection of barium depends, is soluble in the stronger acids, and therefore could not be thrown down in their presence.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING **ANY OR ALL** OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

To the solution add AmCl, AmHO, Am_2CO_3; boil and filter.

Precipitate Ba Ca. Wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4, and filter.		Filtrate Mg Am Na K. Add Am_2HPO_4, shake, filter.	
Precipitate Ba.*	Filtrate Ca. Test by $Am_2C_2O_4$.	Precipitate Mg.	Filtrate Am Na K. Evap. to dryness, ignite, dissolve residue in water. Test for K by $PtCl_4$. Test for Na by flame. Test orig. sol. for Am.

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* It is perhaps scarcely necessary to state that this precipitate is

Note on Classification.—The compounds of barium, calcium, and magnesium, like those of the alkali metals, have many analogies; the carbonate, phosphate, and arseniate of each is insoluble in water, which sufficiently distinguishes them from the members of the class first studied. They possess, however, well-marked differences, so that their separation from each other is easy. The solubility of their hydrates in water marks their connection with the alkali metals; the slightness of that solubility, diminishing as we advance further and further from the alkalies, baryta being most and magnesia least soluble in water, points to their connection with the next class of metals, the hydrates of which are insoluble in water. These considerations must not, however, be over-valued. Though the solubility of their hydrates places barium nearest and magnesium farthest from the alkali metals, the solubility of their sulphates gives them the opposite order, magnesium-sulphate being most soluble, calcium-sulphate next, strontium-sulphate third (strontium is a rarer element, which will be mentioned subsequently), and barium-sulphate insoluble in water. These elements are sometimes spoken of as the metals of the alkaline earths.

Note.—In connection with the bivalence of the metals Barium, Calcium, and Magnesium, it is interesting to note that just as bivalent acidulous radicals give salts containing two atoms of univalent basylous radicals (K_2SO_4, $NaHSO_4$, H_2CO_3, $KNaC_4H_4O_6$), so bivalent basylous radicals yield salts containing two atoms of univalent acidulous radicals, as seen in acetonitrate of barium, $BaC_2H_3O_2NO_3$, a salt which is a definite compound, and not a mere mixture of acetate with nitrate of barium. A very large number of such salts is known.

Distillation.

The water with which, in analysis, solution of a salt or dilution of a liquid is effected should be pure. Well- or river-water is unfit for the purpose, because containing alkaline and earthy salts (about 20 to 60 grains per gallon), derived from the soil through which the water percolates, and rain-water is not unfrequently contaminated with the dust and débris which fall on the roofs whence it is usually collected. Such water is purified by *distillation*, an operation in which the water is by ebullition converted into steam, and the steam condensed again to water in a separate vessel, the fixed earthy and other salts remaining in the vessel in which the water is boiled.

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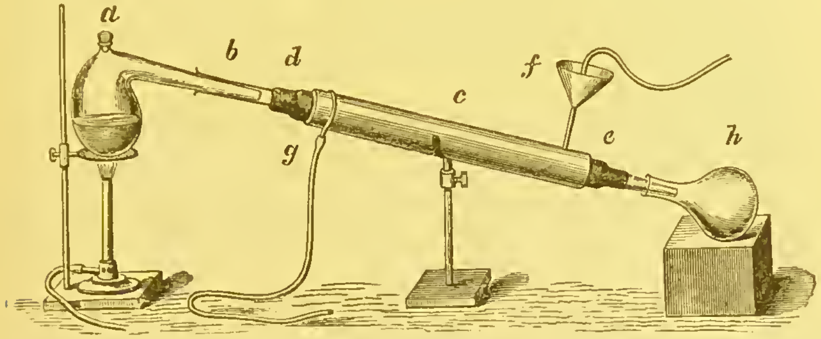
chromate of barium ($BaCrO_4$), as any reader who has carefully gone through the "foregoing analytical reactions" will know. The occurrence of chromate of barium at this particular place, however, and under the circumstances described, is abundant evidence of the presence of barium (in some form or other) in the liquid analyzed—which was a part of the problem to be solved by the operator. Similar remarks apply, of course, to the Ca, which is finally precipitated as oxalate (CaC_2O_4), to Mg, which is thrown out as ammonio-phosphate ($MgAmPO_4$), to Am, Na, and K, and to the elements similarly alluded to in the other subsequent tables for "short" directions for analysis.

On the large scale, ebullition is effected in metal boilers having a hood or head in which is a lateral opening through which passes the steam; on the small scale, either a common glass flask is employed, into the neck of which, by a cork, is inserted a glass tube bent to an acute angle, or a *retort* is used (*a*, Fig. 28) a sort of long-necked Florence flask, dextrously bent near the body by the glass-worker to an appropriate angle (hence the name *retort*, from *retorqueo*, to bend back). *Condensation* is effected by surrounding the lateral steam-tube with cold water. In large stills the steam-tube, or *condensing-worm*, is usually a metal (tin) pipe, twisted into a spiral form for the sake of compactness, and so fixed in a tub that a few inches of one end of the pipe may pass through and closely fit a hole bored near the bottom of the tub. Cold water is kept in contact with the exterior of the pipe, provision being made for a continuous supply to the bottom, while the lighter water heated by the condensing steam runs off from the top of the column. The condenser for a flask or retort may be a simple glass tube of any size, placed within a second much wider tube (a common long, narrow lamp-glass answers very well for experimental operations), the inner tube being connected at the extremities of the wider by bored corks; a stream of water passes into one end of the inclosed space (the end furthest from the retort) through a small glass tube inserted in the cork, and out at the other through a similar tube. The common (Liebig's) form of laboratory condenser is a glass tube three-fourths of an inch wide and a yard long (*b*, Fig. 28), surrounded by a shorter tin or zinc tube (*c*, Fig. 28) two inches in diameter, and having at each extremity a neck, through which the glass tube passes. The ends of the necks of the tin tube, and small portions of glass tube near them, are connected by means of a strip of sheet caoutchouc carefully bound round, or by short, wide India-rubber tubes (*d* and *e*, Fig. 28). An aperture near the lower part of the tin tube provides for the admission of a current of cold water, and a similar aperture near the top (*g*, Fig. 28) allows the escape of heated water. The inner tube may thus constantly be surrounded by cold water, and heated vapors passing through it be perfectly cooled and condensed in any receiver (*h*, Fig. 28).

Fig. 28.



The official Water (*Aqua*, U. S. P.) is to contain "not more than 1 part of fixed impurities in 10,000 parts," and to be so free from organic matter that when tinted rose-red with permanganate of potassium the color should not be destroyed after boiling the fluid for 5 minutes, or, in the case of Distilled Water, after setting the vessel aside, well covered, for ten hours.

In distilling several gallons of water for analytical or medicinal purposes (*Aqua Distillata*, U. S. P.) the first two or three pints should be rejected, because likely to contain ammoniacal and other volatile impurities.

Rectification is the process of redistilling a distilled liquid. *Rectified spirit* is spirit of wine thus treated.

Dry or *destructive distillation* is distillation in which the condensed products are directly formed by the decomposing influence of the heat applied to the dry or non-volatile substances in the retort or still.

EXERCISE.

184. Write from memory two or three paragraphs descriptive of *distillation*.

RECAPITULATION.

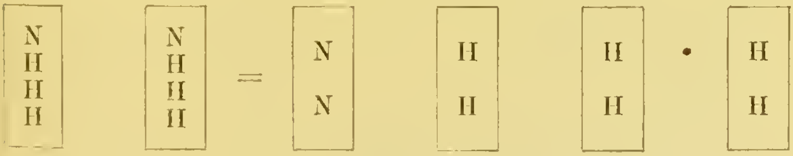
The subject just alluded to (distillation) naturally excites wonder respecting the cause of the physical difference between solid, liquid, and gaseous water. (Common observation will have suggested to the student that the force of heat has much to do with the difference, and if he will turn to the chapter on *latent heat* in any book on Physics he will find that, as already indicated (p. 84), when ice liquefies by heat a very large amount of heat must be used before the slightest rise of temperature occurs. Afterwards the addition of heat makes the water hotter and hotter until one other point is reached (the boiling-point), when here again a great amount of heat is absorbed without causing the slightest rise in temperature. Afterwards more heat makes the gaseous water hotter and hotter, until, like a bar of iron, the steam, under special conditions, is made red hot or white hot.) Different bodies absorb different amounts of heat in changing their physical condition from solid to liquid or liquid to gas (or vapor). The amount is constant for any one body, hence definite comparative numbers may be used for expressing the latent heats of substances.

The absorption of heat at particular (liquefying and vaporizing) points must not be confounded with an analogous physical action, namely, the absorption of heat which goes on when a body is rising in temperature. The amount of this absorption differs with different substances. That is to say, if equal weights of several substances, all at the same temperature, be all heated to a stated higher temperature, very different amounts of fuel will be required. The particular or specific amount in each case is always the same, hence the *specific heats* of substances may be expressed by numbers. See the chapter on "Specific Heat" in any manual of Physics.

But after reading what has been stated respecting the constitution of matter (pp. 42 to 45), the chemical student will, in connection with the subject of distillation, be led, once more, to think over the subject of the molecular constitution of solid, liquid, and gaseous water, and of the molecular condition of bodies generally. As previously stated, little can be told him respecting the molecular condition of solids and liquids, for temperature and pressure affect them unequally, whence we conclude that, though the relation to each other of the molecules of any one substance is constant, this relation is different in different bodies. Different *gases*, however, are not differently affected, but similarly affected by temperature and pressure, whence we conclude that their molecular constitution—the relations of their molecules to one another—is similar.

Another gas, ammonia, has been brought before the reader since the molecular constitution of gases was considered.

A small quantity of ammonia gas inclosed in the upper part of a roughly graduated test-tube over *mercury* (*water* would dissolve it) and exposed to the continuous action of the electric spark by means of wires of platinum fused in the sides of the tube, is decomposed into its elements nitrogen and hydrogen, the bulk of gas operated on being exactly doubled. This expansion is not due to the gaseous molecules receding from each other, but to every two molecules becoming four similar-sized molecules:—



Here each space (rectangular, chiefly for convenience in printing) represents a molecule, and each letter one atom. Each space, if regarded as the side of a double cube, may also, for the moment, represent two volumes—such two volumes yielding, in the decomposition, one volume of nitrogen and three volumes of hydrogen, or the four such volumes of ammonia shown in the diagram yielding two volumes of nitrogen and six volumes of hydrogen.

Remembering that a symbol (of a gas) represents one volume, that *a formula (of a gas) always represents two volumes*, the pupil will now see how full of meaning is such an equation as the following, including, as it does, names of the elements, number of the atoms, nature of the molecules, number of the molecules, weights of atoms of the molecules, and therefore weights of bulks of the bodies, and extent of expansion in the disunion of the elements, and therefore their extent of contraction in the act of union:—

$$2NH_3 = N_2 + 3H_2.$$

AT THIS STAGE THE LEARNER IS AGAIN RECOMMENDED TO READ THE PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY, AND TO RETURN TO THEM FROM TIME TO TIME UNTIL THEY ARE THOROUGHLY COMPREHENDED.

ZINC, ALUMINIUM, IRON.

These three elements are classed together for analytical convenience rather than for more general analogies.

ZINC.

Symbol Zn. Atomic weight 64.9.

Source.—Zinc is tolerably abundant in nature as sulphide (ZnS) or *blende*, and carbonate ($ZnCO_3$), or *calamine* (from *calamus*, a reed, in allusion to the appearance of the mineral). The ores are roasted to expel sulphur, carbonic acid gas, and some impurities, and the resulting oxide distilled with charcoal, when the metal vaporizes and readily condenses. Zinc is a brittle metal, but at a temperature somewhat below 300° F. is malleable, and may be rolled into thin sheets. Above 400° it is again brittle, and may then be pulverized. At 773° F. it melts, and at a bright red heat is volatile. Zinc in exceptionally fine powder ignites spontaneously, especially if damp or if stored in a warm place.

Uses.—Its use as a metal is familiar; alloyed with nickel and copper it yields german silver, with twice its weight of copper forms common brass, and as a coating on iron (the so-called *galvanized* iron) greatly retards the formation of rust. Most of the salts of zinc are prepared directly or indirectly from the metal (*Zincum*, U. S. P.).

Quantivalence.—The atom of zinc is bivalent, Zn''.

Molecular Weight.—Some remarks on this point will be made under Mercury.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

Sulphate of Zinc.

First Synthetical Reaction.—Heat zinc (4 parts) with water (20 parts) and sulphuric acid (3 fl. parts) in a test-tube (or larger vessel) until gas ceases to be evolved; solution of sulphate of zinc ($ZnSO_4$) results. Filter (to separate the particles of lead, carbon, etc., commonly contained in sheet zinc); and concentrate the solution in an evaporating-dish; on cooling, colorless, transparent, prismatic crystals of Sulphate of Zinc ($ZnSO_4,7H_2O$) are deposited (*Zinci Sulphas*, U. S. P.).

$$\underset{\text{Zinc.}}{Zn_2} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{2H_2SO_4} + \underset{\text{Water.}}{xH_2O} = \underset{\substack{\text{Sulphate of}\\ \text{zinc.}}}{2ZnSO_4} + \underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Water.}}{xH_2O}$$

Zinc does not displace hydrogen from the sulphuric acid alone, nor from the water alone, yet the mixture affords hydrogen. The probable explanation is that as sulphuric acid combines with several different quantities of water to form definite hydrous compounds (H_2SO_4,H_2O; $H_2SO_4,2H_2O$; etc.), it is one of these that is decomposed with elimination of hydrogen. At present we can only say that an unknown (x) amount of water is required in the reaction.

Note.—This reaction affords hydrogen and sulphate of zinc; it also develops electricity. Of several methods of evolving hydrogen, it is the most convenient; of the two or three means of preparing sulphate of zinc, it is the most commonly employed; and of the many reactions which may be utilized in the development of dynamic electricity, it is at present the cheapest and most manageable. The apparatus in which the reaction is effected differs according to the requirements of the operator: if the sulphate of zinc alone is wanted, an open dish is all that is necessary, the action being, perhaps, accelerated by heat; if hydrogen, a closed vessel and delivery-tube; if electricity, square vessels called cells, and certain complementary materials, forming altogether what is termed a battery. In each operation for one product, the other two are commonly wasted. It would not be difficult for the operator, as a matter of amusement, to construct an apparatus from which all three products should be collected.

Purification.—Impure sulphate of zinc may be purified in the same manner as impure chloride (see next reaction).

Sulphate of zinc is isomorphous with sulphate of magnesium, and like that salt, loses six-sevenths of its water of crystallization at 212° F.

Chloride of Zinc.

Second Synthetical Reaction.—Dissolve zinc in hydrochloric acid mixed with half its bulk of water; the resulting solution contains chloride of zinc. Evaporate the liquid till no more steam escapes; Chloride of Zinc ($ZnCl_2$) in a state of fusion remains, and on cooling is obtained as an opaque white solid (*Zinci Chloridum*, U. S. P.).

It is soluble in water, alcohol, or ether.

$$\underset{\text{Zinc.}}{Zn_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} = \underset{\substack{\text{Chloride}\\ \text{of zinc.}}}{2ZnCl_2} + \underset{\text{Hydrogen.}}{2H_2}$$

This reaction is analogous to that previously prescribed. The Burnett deodorizing or disinfecting liquid is solution of chloride of zinc.

Purification of Chloride or Sulphate of Zinc.—Zinc sometimes contains traces of iron or lead; and these, like zinc, are dissolved by most acids, with formation of soluble salts; they may be recognized in the liquids by applying the tests described hereafter to a little of the solution in a test-tube. Should either be present in the above solution, a little chlorine-water is added to the liquid till the odor of chlorine is permanent, and then the whole well shaken with some hydrate of zinc or the common official "carbonate" of zinc (really hydrato-carbonate—see p. 131). In this way iron is precipitated as ferric hydrate, and lead as peroxide :—

$$\underset{\text{Ferrous chloride.}}{{}^{*}2FeCl_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Ferric chloride.}}{{}^{*}Fe_2Cl_6}$$

$$\underset{\substack{\text{Ferric}\\ \text{chloride.}}}{Fe_2Cl_6} + \underset{\substack{\text{Carbonate}\\ \text{of zinc.}}}{3ZnCO_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\substack{\text{Chloride}\\ \text{of zinc.}}}{3ZnCl_2} + \underset{\substack{\text{Carbonic}\\ \text{acid gas.}}}{3CO_2}$$

$$\underset{\substack{\text{Chloride}\\ \text{of lead.}}}{PbCl_2} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\substack{\text{Carbonate}\\ \text{of zinc.}}}{2ZnCO_3} = \underset{\substack{\text{Peroxide}\\ \text{of lead.}}}{PbO_2} + \underset{\substack{\text{Chloride}\\ \text{of zinc.}}}{2ZnCl_2} + \underset{\substack{\text{Carbonic}\\ \text{acid gas.}}}{2CO_2}$$

In the British Pharmacopœia the presence of impurities in the zinc is assumed, and the process of purification just described incorporated with the process of preparation of *Zinci Chloridum*, *Liquor Zinci Chloridi*, and *Zinci Sulphas*. In the purification of the sulphate of zinc, the action of chlorine on any ferrous sulphate will result in the formation of ferric sulphate as well as ferric chloride :—

$$6FeSO_4 + Cl_6 = 2(Fe_2 3SO_4) + Fe_2Cl_6;$$

carbonate of zinc will then give chloride as well as sulphate of zinc, and thus the whole quantity of sulphate of zinc be slightly contaminated by chloride. On evaporating and crystallizing, however, the chloride of zinc will be retained in the mother-liquor. This process admits of *general* application.

For *Liquor Zinci Chloridi*, B. P., 1 pound of zinc is placed in a mixture of 44 fluidounces of hydrochloric acid and 20 of water, the mixture ultimately warmed until no more gas escapes, filtered into a bottle, chlorine-water added until the liquid after shaking smells fairly of chlorine, about half an ounce or somewhat more of carbonate of zinc shaken up with the solution until a brown precipitate (of ferric hydrate or peroxide of lead, or both) appears, the whole filtered, and the filtrate evaporated to 40 fluidounces. One fluidounce contains 366 grains of chloride of zinc. If there is reason to believe that neither iron nor lead is present in the zinc, the treatment with chlorine-water and carbonate of zinc may be omitted. The *Liquor Zinci Chloridi*, U. S. P., is prepared by a somewhat similar process, nitric acid, however, is used instead of chlorine-water; the solution contains "about 50 per cent. of the salt ($ZnCl_2$)," sp. gr. 1.555. It is miscible with alcohol in all proportions, indicating absence of basic chloride of zinc.

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* It will be noticed that the iron is represented, in these equations, as exerting both bivalent and trivalent activity; this will be alluded to when iron comes under consideration.

Bromide of Zinc, $ZnBc_2$ (*Zinci Bromidum*, U. S. P.) may be made by the action of zinc on hydrobromic acid and evaporation to dryness. It is a white powder, but may be sublimed in needles.

Iodide of Zinc, ZnI_2 (*Zinci Iodidum*, U. S. P.) may be made from its elements. It is a white powder, but when volatilized condenses in acicular prisms.

Carbonate of Zinc.

Third Synthetical Reaction.—To solution of any given quantity of sulphate of zinc in twice its weight of water (in a test-tube, evaporating-basin, or other large or small vessel), add about an equal quantity of carbonate of sodium, also dissolved in twice its weight of water, and boil; the resulting white precipitate is so-called Carbonate of Zinc (*Zinci Carbonas*, B. P., *Zinci Carbonas Præcipitatus*, U. S. P.), a mixture of carbonate ($ZnCO_3$) and hydrate ($Zn2HO$), in the proportion of two molecules of the former and three of the latter. It may be washed, drained, and dried in the usual manner. It is used in the arts under the name of *zinc-white.*

$$\underset{\substack{\text{Sulphate}\\\text{of zinc.}}}{5ZnSO_4} + \underset{\text{Water.}}{3H_2O} + \underset{\substack{\text{Carbonate}\\\text{of sodium.}}}{5Na_2CO_3} = \underset{\substack{\text{Official carbonate}\\\text{of zinc.}}}{2ZnCO_3,3ZnH_2O_2} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

$$+ \underset{\substack{\text{Sulphate}\\\text{of sodium.}}}{5Na_2SO_4}$$

Acetate of Zinc.

Fourth Synthetical Reaction.—Collect in a filter the precipitate obtained in the last reaction, wash with distilled water, and dissolve a portion in strong acetic acid; the resulting solution contains acetate of zinc ($Zn2C_2H_3O_2$), and, on evaporating and setting aside for a day, yields lamellar pearly crystals ($Zn2C_2H_3O_2,3H_2O$) (*Zinci Acetas*, U. S. P.).

$$\underset{\text{Official carbonate of zinc.}}{2ZnCO_3,3ZnH_2O_2} + \underset{\text{Acetic acid.}}{10HC_2H_3O_2} = \underset{\text{Acetate of zinc.}}{5(Zn''2C_2H_3O_2)} + \underset{\text{Water.}}{8H_2O} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Another process consists in digesting oxide of zinc in acetic acid, heating the mixture to boiling-point, filtering while hot, and setting aside the clear solution to crystallize.

Oxide of Zinc.

Fifth Synthetical Reaction.—Dry the remainder of the precipitated carbonate (by placing the open filter on a plate over a dish of water kept boiling), and then heat it in a small crucible till it ceases to effervesce on the addition of water and acid to trial samples taken out of the crucible from time to time; the product is Oxide of Zinc (*Zinci Oxidum*, U. S. P.).

$$\underset{\text{Official carbonate of zinc.}}{2ZnCO_3,3ZnH_2O_2} = \underset{\text{Oxide of zinc.}}{5ZnO} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Note.—This oxide is yellow while hot, and of a very pale yellow or slight buff tint when cold, not actually white, like the oxides prepared by the combustion of zinc in air. The latter variety occurs in commerce under the name of Hubbuck's oxide of zinc. Its preparation can only be practically accomplished on the large scale, but the chief features of the action may be observed by heating a piece of zinc on charcoal in the blowpipe-flame (Fig. 29) till it burns; flocks escape, float about in the air, and slowly fall. These are the old *Flores Zinci*, *Lana Philosophica*, or *Nihilum Album*.

Fig. 29.

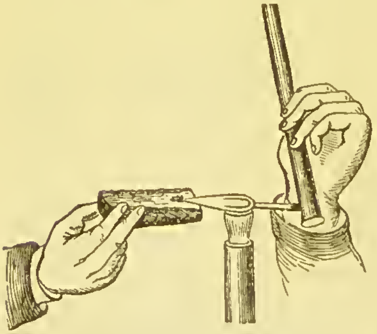
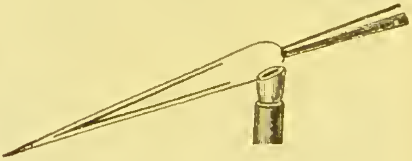


Fig. 30.



The Blowpipe.

A clear blowpipe-flame consists more or less of two portions (see Fig. 30), an inner cone, at the apex of which are hot gases greedy of oxygen, and an outer cone, at the apex of which is excess of hot oxygen. At the latter point oxidizable metals, etc. are readily oxidized, as in the foregoing experiment, and that part of the flame is therefore termed the *oxidizing* flame; in the inner flame oxides and other compounds (a grain of acetate of lead may be employed for illustration) are reduced to the metallic state, hence that part is termed the *reducing* flame. A blowpipe-flame is much altered in character by slight variations in the position of the nozzle of the blowpipe, by the form of the nozzle, by the force with which air is expelled from the blowpipe, and by the character of the jet of gas.

Valerianate of Zinc.

Sixth Synthetical Reaction.—Valerianate of Zinc ($Zn2C_5H_9O_2,H_2O$) (*Zinci Valerianas*, U. S. P.) is prepared by mixing strong solutions of sulphate of zinc and valerianate of sodium, cooling, separating the white pearly crystalline matter, evaporating at 200° F. to a low bulk, cooling, again separating the lamellar crystals, washing the whole product with a small quantity of cold distilled water, draining, and drying by exposure to air at ordinary temperatures. Valerianate of zinc is soluble in ether, alcohol, or hot water.

$$\underset{\text{Sulphate of zinc.}}{ZnSO_4} + \underset{\text{Valerianate of sodium.}}{2NaC_5H_9O_2} = \underset{\text{Sulphate of sodium.}}{Na_2SO_4} + \underset{\text{Valerianate of zinc.}}{Zn2C_5H_9O_2}$$

Note.—The compounds of zinc described in the foregoing six reactions are the only ones mentioned in the British Pharmacopœia; the processes are also those of that work. *Sulphide and Hydrate of Zinc* are mentioned in the following analytical paragraphs. The formula of *Sulphite of Zinc* is $ZnSO_3,3H_2O$.

(*b*) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—To solution of a zinc salt (sulphate, for example) in a test-tube, add solution of sulphydrate of ammonium (NH_4HS); white sulphide of zinc (ZnS) is precipitated, insoluble in acetic, but soluble in the stronger acids.

Note.—This is the only white sulphide that will be met with. Its formation, on the addition of the sulphydrate of ammonium, is therefore highly characteristic of zinc. If the zinc salt contains iron or lead as impurities, the precipitate will have a dark appearance, the sulphides of those metals being black. Hydrate of aluminium, which is also white and precipitated by sulphydrate of ammonium, is the only substance sulphide of zinc is likely to be mistaken for, and *vice versâ:* but, as will be seen immediately, there are good means of distinguishing these from each other.

Second Analytical Reaction.—To solution of a zinc salt add solution of ammonia; white hydrate of zinc (Zn2HO) is precipitated. Add excess of ammonia; the precipitate is redissolved.

This reaction at once distinguishes a zinc salt from an aluminium salt, hydrate of aluminium being insoluble, practically, in ammonia.

Other Analytical Reactions.—The fixed alkali-hydrates afford a similar reaction to that just mentioned, the hydrate of zinc redissolving if the alkali is free from carbonate.——Carbonate of ammonium yields a white precipitate of carbonate and hydrate, soluble in excess.——The fixed alkaline carbonates give a similar precipitate, which is not redissolved if the mixed solution and precipitate be well boiled.——Ferrocyanide of potassium precipitates white ferrocyanide of zinc (Zn_2FeCy_6).

Sulphate of magnesium, which is isomorphous with, and indistinguishable in appearance from, sulphate of zinc, is not precipitated from its solutions either by ferrocyanide of potassium or sulphydrate of ammonium.

Antidotes.—There are no efficient chemical means of counteracting the poisonous effects of zinc. Large doses, fortunately, act as powerful emetics. If vomiting has not occurred, or apparently to an insufficient extent, solution of carbonate of sodium (common washing salt), immediately followed by white of egg and demulcents, may be administered.

QUESTIONS AND EXERCISES.

185. Give the sources and uses of metallic zinc.

186. Explain by a diagram what occurs when zinc is dissolved in diluted sulphuric acid.

187. How may solutions of Chloride and of Sulphate of Zinc be purified from salts of iron? Give equations descriptive of the reactions.

188. State the formula of Carbonate of Zinc, and illustrate by a diagram the reaction which takes place in its production.

189. Give an equation showing the formation of Acetate of Zinc.

190. In what respect does Oxide of Zinc, resulting from the ignition of the carbonate, differ from that produced during the combustion of the metal?

191. How is Valerianate of Zinc prepared?

192. What are the properties of Valerianate of Zinc?

193. Name the more important tests of Zinc.

194. How would you distinguish, chemically, between solutions of Sulphate of Zinc and Alum?

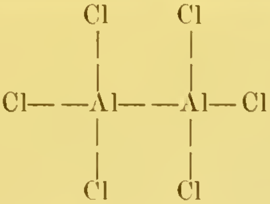
195. Describe the treatment in cases of poisoning by the salts of zinc.

196. Give reactions distinguishing Sulphate of Zinc from Sulphate of Magnesium.

ALUMINIUM.

Symbol Al. Atomic weight 27.

Note.—In the formulæ of aluminium salts it will be observed that to one atom of metal there are three atoms of other univalent radicals; hence, apparently, the atom of aluminium is trivalent, Al'''. But possibly it is quadrivalent; for one molecule of aluminium compounds includes two atoms of the metal, three-fourths only of whose power may be supposed to be exerted in retaining the other constituents of the molecule, the remaining fourth enabling the aluminium atoms themselves to keep together. This is graphically shown in the following formula of chloride of aluminium (Al_2Cl_6) from Frankland's "Lecture Notes for Chemical Students," which



$$\begin{array}{ccccc} & Cl & & Cl & \\ & | & & | & \\ Cl - & Al & - & Al & - Cl \\ & | & & | & \\ & Cl & & Cl & \end{array}$$

represents each aluminium atom as a body having four arms or bonds, three of which are engaged in grasping the arms of univalent chlorine atoms, while the fourth grasps the corresponding arm of its brother aluminium atom. Such graphic formulæ, as they are called, are useful in facilitating the acquirement of hypotheses regarding the constitution of chemical substances, especially if the error be avoided of supposing that they are pictures either of the position or absolute power of atoms in a molecule, or indeed, the true representation of a molecule at all; for on this point man knows little or nothing.

Source.—Aluminium is very abundant in nature, chiefly as silicate, in clays, slate, marl, granite, basalt, and a large number of minerals. *Mica* consists chiefly of silicates of aluminium, iron, and potassium. *Rotten-stone* is a soft and friable aluminium silicate containing a little organic matter. The sapphire and ruby are almost pure oxide of aluminium. The metal aluminium is obtained from the double chloride of aluminium and sodium, by the action of metallic sodium, the source of the chloride being the mineral *bauxite*—a more or less ferruginous hydrate of aluminium.

Aluminium-bronze is an alloy of ten parts of aluminium with ninety of copper.

Alum (*Alumen*, U. S. P.), a double sulphate of aluminium and potassium ($Al_23SO_4,K_2SO_4,24H_2O$), may be obtained from aluminous schist (from *σχιστὸς*, *schistos*, divided), a sort of pyritous slate or shale, by exposure to air; oxidation and chemical change produce sulphate of aluminium, sulphate of iron, and silica, from the silicate of aluminium and bisulphide of iron (iron pyrites) originally present in the shale. The sulphate of aluminium and sulphate of iron are dissolved out of the mass by water, and sulphate of potassium added; on concentrating the liquid, alum crystallizes out, while the more soluble iron salt remains in the mother liquor.

Alum is also prepared by directly decomposing the silicate of aluminium in the calcined shale of the coal-measures by hot sulphuric acid, sulphate of potassium being added from time to time until a solution strong enough to crystallize is obtained. The liquid well agitated during cooling deposits alum, in minute crystals, termed *alum-flour*, which is afterwards recrystallized.

Alums.—There are several *alums*, iron or chromium taking the place of aluminium, and ammonium or sodium that of potassium, all crystallizing in an eight-sided form, the octahedron—a sort of double pyramid. These are apparently alike in chemical constitution, and their general formula (M = either metal) is $M'''_2 3SO_4, M'_2SO_4, 24H_2O$. The alum of the manufacturer commonly occurs in colorless, transparent, octahedral crystals, massed in lumps, which are roughly broken up for trade purposes, but still exhibit the faces of octahedra. It is liable to contain sulphate of ammonium or sulphate of potassium, according as one or other is the cheaper.

Sulphate of Aluminium ($Al_2 3SO_4, 9H_2O$), or *Alum Cake*, prepared from natural silicates in the manner just described, is a common article of trade, serving most of the manufacturing purposes for which alum was formerly employed. It is official in the United States Pharmacopœia (*Aluminii Sulphas*). It may be made by dissolving hydrate of aluminium in diluted sulphuric acid, with subsequent removal of water by evaporation.

$$Al_2 6HO + 3H_2SO_4 = Al_2 3SO_4 + 6H_2O.$$

The hydrate of aluminium (*Aluminii Hydras*, U. S. P.) is to be prepared by the addition of solution of alum to solution of carbonate of sodium, the precipitated hydrate being collected on a filter and well washed.

$$Al_2 3SO_4, K_2SO_4 + 3Na_2CO_3 + 3H_2O = Al_2 6HO + K_2SO_4 + 3Na_2SO_4 + 3CO_2.$$

Preparation of Alum.—Prepare alum by heating a small quantity of powdered pipe-clay (silicate of aluminium) with about twice its weight of sulphuric acid for some time, dissolving out the resulting sulphate of aluminium and excess of sulphuric acid by water, and adding ammonia to the clear filtered solution only until, after well stirring, the excess of acid is neutralized. (If too much ammonia be added, the hydrate of aluminium precipitated when the ammonia is first poured in will not be redissolved on well mixing the whole. Perhaps the readiest indication of neutrality in this and similar cases is the presence of a little precipitate after stirring and warming the mixture.) On evaporating the clear solution, crystals of alum are obtained.

The *Ammonio-ferric Alum* or *Ammonio-ferric Sulphate* of American pharmacy (*Ferri et Ammonii Sulphas*, U. S. P.) may be made by adding sulphate of ammonium to a hot solution of persulphate of iron, and setting the liquid aside to crystallize. It forms pale violet octahedral crystals expressed by the formula Fe_23SO_4, $(NH_4)_2SO_4,24H_2O$.

Dried Alum (*Alumen Exsiccatum*, U. S. P.) is alum from which the water of crystallization has been expelled by heat, the temperature not exceeding 205° C. or 400° F. By calculation from the molecular weight of alum, it will be found that the salt contains between 45 and 46 per cent. of water. At temperatures above 400° ammonium alum is decomposed, sulphate of ammonium and sulphuric anhydride escaping, and pure oxide of aluminium (Al_2O_3) remaining. Dried alum rapidly reabsorbs water from the atmosphere.

Roche alum, or *Rock alum* (*roche*, French, rock), is the name of an impure native variety of alum containing iron. The article sold under this name is sometimes an artificial mixture of common alum with oxide of iron.

REACTIONS HAVING ANALYTICAL INTEREST.

First Analytical Reaction.—To a solution of an aluminium salt (alum, for example, which contains sulphate of aluminium) add sulphydrate of ammonium (NH_4HS); a gelatinous white precipitate of hydrate of aluminium falls:—

$$Al_23SO_4 + 6AmHS + 6H_2O = Al_26HO + 3Am_2SO_4 + 6H_2S.$$

Second Analytical Reaction.—To a solution of alum add ammonia, NH_4HO; hydrate of aluminium falls: add excess of ammonia; the precipitate is, practically, insoluble.

Principle of Dyeing by help of Mordants.—The precipitated hydrate of aluminium, or alumina, has great affinity for vegetable coloring-matters and also for the fibre of cloth. Once more perform the above experiment, but before adding the ammonia introduce some decoction of logwood, solution of cochineal, or other similar colored liquid, into the test-tube. Add now the ammonia, and set the tube aside for the alumina to fall; the latter takes down with it all the coloring principle. In dye-works the fabrics are passed through liquids holding the alumina but weakly in solution, and then through the coloring solutions; from the first bath the fibres abstract alumina, and from the second the alumina abstracts coloring-matter. Some other metallic hydrates, notably those of tin and iron, resemble alumina in this property; they are all termed *mordants* (from *mordens*, biting); the substances they form with coloring-matters have the name of *lakes*.

Third Analytical Reaction.—To the alum add solution of potash; again hydrate of aluminium falls. Add excess of potash, and agitate; the precipitate dissolves.

Hydrate of aluminium may be precipitated from this solution by neutralizing the potash with hydrochloric acid, and adding ammonia until, after shaking, the mixture has an ammoniacal smell, or by adding solution of chloride of ammonium to the potash liquid. But the former way is the better; for it is difficult to know when a sufficiency of the chloride of ammonium has been poured in, whereas reaction with blue and red litmus-paper at once enables the operator to know when excess of hydrochloric acid or ammonia has been added.

Alkaline phosphates, arseniates, and salts of other acidulous radicals also decompose solutions of aluminium salts and produce insoluble compounds of that metal, with the several acidulous radicals, but the resulting precipitates are of no special interest.

QUESTIONS AND EXERCISES.

197. What is there remarkable about the quantivalence of aluminium?

198. Practically, what is the quantivalence of the atom of aluminium?

199. Enumerate the chief natural compounds of aluminium.

200. Write down a formula which will represent either of the Alums.

201. Which *alum* is official, and commonly employed in the arts?

202. State the source and explain the formation of alum.

203. What is the crystalline form of alum? Work a sum showing how much Dried Alum is theoretically producible from 100 pounds of alum. Ans. 52 lbs. 6 oz.

204. Show by figures how ordinary ammonium alum is capable of yielding 11.356 per cent. of alumina.

205. Why are aluminium compounds used in dyeing?

206. How are salts of aluminium analytically distinguished from those of zinc?

IRON.

Symbol Fe. Atomic weight 55.9.

Sources.—Compounds of iron are abundant in nature. *Magnetic Iron Ore*, or *Loadstone* (*Lodestone* or *Leadstone*, from the Saxon *lædan*, to lead, in allusion to its use, or rather to the use of magnets made from it, in navigation), is the chief ore from which Swedish iron is made; it is a mixture of ferrous and ferric oxides (FeO,Fe_2O_3). Much of the Russian iron is made from *Specular Iron Ore* (from *speculum*, a mirror, in allusion to the lustrous nature of the crystals of this mineral). This and *Red Hæmatite* (from *αἷμα, haima*, blood, so named from the color of its streak), an ore raised in Lancashire, are composed of ferric oxide only (Fe_2O_3). *Brown Hæmatite*, an oxyhydrate, is the source of much of the French iron. *Spathic Iron Ore* (from *spatha*, a slice, in allusion to the lamellar structure of the ore) is a ferrous carbonate ($FeCO_3$). An impure ferrous carbonate forms the *Clay Ironstone*, whence most of the English iron is derived. The chief Scotch ore is also an impure carbonate, containing much bituminous matter; it is known as *Black Band*. *Iron Pyrites* (from πῦρ, *pur*, fire, in allusion to the production of sparks when sharply struck) (FeS_2) is a yellow lustrous mineral, of use only for its sulphur. As met with in coal it is commonly termed *coal brasses*. Ferrous carbonate ($FeCO_3$), chloride ($FeCl_2,4H_2O$), and sulphate ($FeSO_4,7H_2O$) sometimes occur in springs, the water of which is hence termed *chalybeate* (*chalybs*, steel).

Process.—Iron is obtained from its ores by processes of roasting, and reduction of the resulting impure oxide with coal or charcoal in the presence of chalk, the latter uniting with the sand, clay, etc. to form a fusible slag. The *cast iron* thus produced may be converted into *wrought iron* by burning out the 4 or 5 per cent. of carbon, silicon, and other impurities present, by oxidation in a furnace, an operation which is termed *puddling*. *Steel* is iron containing from one to two per cent. of carbon, and is made by the now celebrated Bessemer process of burning out from cast iron the variable amount of carbon it contains, and then adding melted iron containing a known proportion of carbon. The official varieties of the metal are "metallic iron, in the form of fine, bright, and non-elastic wire" (*Ferrum*, U. S. P.); and "wrought iron in the form of wire or nails free from oxide" (*Ferrum*, B. P.), the conditions in which it is most easily employed for conversion into its compounds. In the form of a fine powder (see 17 Reac.) metallic iron is employed as a medicine.

Properties.—The specific gravity of pure iron is 7.844, of the best bar iron 7.7; its color is bluish-white or gray. Bar iron requires the highest heat of a wind-furnace for fusion, but below that temperature assumes a pasty consistence, and in that state two pieces may be joined or *welded* (Germ. *wellen*, to join) by the pressure of blows from a hammer. A little sand thrown on to the hot metal facilitates this operation by forming with the superficial oxide of iron a fusible slag, which is dispersed by the blows: the purely metallic surfaces are thus better enabled to come into thorough contact and enter into perfect union. Iron is highly ductile, and of all common metals possesses the greatest amount of tenacity. At a high temperature it burns in the air, forming oxide of iron. *Rust of iron* is chiefly red oxide of iron, with a little ferrous oxide and carbonate; it is produced by action of the moist carbonic acid of the air and subsequent oxidation. Steam passed over scrap iron heated to redness gives hydrogen gas and black oxide of iron. Iron exposed at a high temperature to oxidation by a limited amount of steam (Barff) or air (Bower) becomes coated with magnetic oxide of so closely coherent and adherent a nature that the metal is permanently protected from alteration by atmospheric and many other influences.

Quantivalence.—Iron combines with other elements and radicals in two proportions; those salts in which the atom of iron appears to possess inferior affinities (in which the other radicals are in the less amount) are termed *ferrous*, the higher being *ferric* salts. In the former the iron exerts bivalent (Fe''), in the latter trivalent activity (Fe''' or Fe_2^{VI}).

The atom of iron is also sometimes considered to be sexivalent, on account of the analogy of its compounds with those of chromium, which is sexivalent, if the formula of its fluoride (CrF_6) be correct, and because the composition of *ferrate of potassium* (K_2FeO_4), a deep purple salt obtained on passing chlorine through a concentrated solution of potash in which fresh ferric hydrate is suspended, is best explained on the assumption of the sexivalence of its iron.

Why the quantivalence of the atom of iron should vary is not at present known.

The Nomenclature of Iron Salts.—For educational and descriptive purposes the two classes of iron compounds are very conveniently spoken of as *ferrous* and *ferric*, the syllable "*ferr*" common to all indicating their allied ferruginous character, the syllables *ous* and *ic* indicating the lower and higher class respectively—functions fulfilled by these two syllables in other similar cases (sulphurous and sulphuric, mercurous and mercuric). Officially the iron salts are known by other names, thus, *Sulphate of Iron* (*Ferri Sulphas*) and *Phosphate of Iron* (*Ferri Phosphas*), names which are chemically inexplicit, for there are two sulphates, and two phosphates, and the terms do not define which salt is intended. Consistency and uniformity would demand that the names Ferrous Sulphate, Ferrous Phosphate, or similar terms, should be employed. Practically, however, the old names cause no confusion, inasmuch as, commonly, only one sulphate, phosphate, etc. are used in medicine; moreover, the higher salts usually have the prefix *per* attached (as persulphate, perchloride). These names are already well known, can be easily rendered in Latin, and then admit of simple abbreviations and adaptations such as are employed in prescriptions, advantages not possessed by the more rational terms. While, therefore, the comprehension of the chemistry of iron is rendered simple and intelligible by the use of the terms ferrous and ferric, the employment of older and less definite names may very well be continued in pharmacy as being practically more convenient.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

FERROUS SALTS.

Green Sulphate of Iron. Ferrous Sulphate.

First Synthetical Reaction.—Place iron (small tacks) in sulphuric acid diluted with eight times its bulk of water (in a test-tube, basin, or other vessel of any required size), accelerating the action by heat until effervescence ceases.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Water.}}{xH_2O} = \underset{\text{Ferrous sulphate.}}{2FeSO_4} + \underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Water.}}{xH_2O}$$

The solution contains what is generally known as Sulphate of Iron, that is, Ferrous Sulphate, the lower of the two sulphates, and will yield crystals of that substance $(FeSO_4,7H_2O)$ (*Ferri Sulphas*, U. S. P.) on cooling or on further evaporation; or if the hot concentrated solutions be poured into alcohol, the mixture being well stirred, the sulphate is at once thrown down in minute crystals (*Ferri Sulphas Præcipitatus*, U. S. P.). At a temperature of 300° F. ferrous sulphate loses six-sevenths of its water, and becomes the *Ferri Sulphas Exsiccatus*, U. S. P., a salt used in the preparation of *Pilulæ Aloes et Ferri*, U. S. P. (See analogous zinc reaction on p. 129.)

Other Sources of Ferrous Sulphate.—In the laboratory ferrous sulphate is often obtained as a by-product in making sulphuretted hydrogen:—

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

In manufactories it occurs as a by-product in the decomposition of aluminous shale, as already noticed (p. 135).

Ten grains of granulated sulphate of iron dissolved in one ounce of water constitute "Solution of Sulphate of Iron," B. P. "The solution should be recently prepared."

Notes.—Ferrous sulphate is sometimes termed *green vitriol.* Vitriol (from *vitrum*, glass) was originally the name of any transparent crystalline substance, but afterwards restricted to the sulphates of zinc, iron, and copper, which were, and still are, occasionally known as white, green, and blue vitriol. *Copperas* (probably originally *copper-rust*, a term applied to verdigris and other green incrustations of copper) is another name for this sulphate of iron, sometimes distinguished as *green copperas*, sulphate of copper being blue copperas. Solid sulphate of iron is a constituent of *Pilulæ Aloes et Ferri*, B. P. Ferrous sulphate forms a light-green double salt with sulphate of ammonium.

Ferrous sulphate, when exposed to the air, gradually turns brown through absorption of oxygen, ferric oxysulphate (Fe_2O2SO_4) being formed. The latter is not completely dissolved by water, owing to the formation of a still lower insoluble oxysalt $(Fe_4O_5SO_4)$ and soluble ferric sulphate, $5(Fe_2O2SO_4) = Fe_4O_5SO_4 + 3(Fe_23SO_4)$.

Iron heated with undiluted sulphuric acid gives sulphurous acid gas and ferrous sulphate:—

$$Fe_2 + 4H_2SO_4 = 2SO_2 + 2FeSO_4 + 4H_2O.$$

Carbonate of Iron. Ferrous Carbonate.

Second Synthetical Reaction.—To solution of ferrous sulphate, boiling, in a test-tube, add solution of bicarbonate of sodium $(NaHCO_3)$ in recently boiled water; a white precipitate of ferrous carbonate ($FeCO_3$) is thrown down, rapidly becoming light green, bluish green, and, after a long, time, red, through absorption of oxygen, evolution of carbonic acid gas, and formation of ferric oxyhydrate.

$FeSO_4$	+	$2NaHCO_3$	=	$FeCO_3$	+	Na_2SO_4	+	H_2O	+	CO_2
Ferrous sulphate.		Bicarbonate of sodium.		Ferrous carbonate.		Sulphate of sodium.		Water.		Carbonic acid gas.

Saccharated Carbonate of Iron.—The above precipitate, rapidly washed with hot, well-boiled distilled water, and the moist powder mixed with sugar, and quickly dried—in short, all possible precautions taken to avoid exposure to air—forms the saccharated carbonate of iron (*Ferri Carbonas Saccharatus*, U. S. P.).

The official proportions are 10 of the sulphate dissolved in 40 of hot water, and 7 of the bicarbonate dissolved in 100 of warm water, and each filtered. The former is then added to the latter in a flask, the mixture shaken, the precipitate washed by decantation until the washings give only a very slight turbidity with chloride of barium, drained, and while still somewhat moist mixed with 16 parts of sugar, and finally dried over a water-bath.

Carbonate of iron, mixed with honey and sugar, forms the *Massa Ferri Carbonatis*, U. S. P.

Ferrous carbonate is said to be more easily dissolved in the stomach than any other iron preparation. It is so unstable and prone to oxidation, that it must be washed in water containing no dissolved air and mixed with the sugar (which protects it from oxidation) as quickly as possible. In making the official compound mixture of iron (*Mistura Ferri Composita*, U. S. P.), "Griffith's mixture," the various ingredients, including the carbonate of potassium, should be placed in a bottle of the required size, space being left for the crystals or solution of ferrous sulphate, which should be added last, the bottle immediately filled up with the rose-water, and securely corked; the minimum of oxidation is thus insured. *Pilulæ Ferri Compositæ*, U. S. P., is made from myrrh, carbonate of soda, sulphate of iron, and syrup; carbonate of iron is gradually formed.

$FeSO_4$	+	K_2CO_3	=	$FeCO_3$	+	K_2SO_4
Ferrous sulphate.		Carbonate of potassium.		Ferrous carbonate.		Sulphate of potassium.

Arseniate of Iron. Ferrous Arseniate.

Third Synthetical Reaction, by which the lower arseniate of iron, ferrous arseniate (*Ferri Arsenias*, B. P.) ($Fe_3 2AsO_4$), partially oxidized, is formed. This will be noticed again under Arsenicum.

Phosphates of Iron. *a.* Ferrous Phosphate.

Fourth Synthetical Reaction.—To solution of ferrous sulphate in a test-tube add a little solution of acetate of sodium, then solution of phosphate of sodium; the lower phosphate of iron, ferrous phosphate (Fe_32PO_4) is precipitated (*Ferri Phosphas*, B. P.).

b. Ferric phosphate (see page 152).

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{3FeSO_4} + \underset{\substack{\text{Phosphate of}\\\text{sodium.}}}{2Na_2HPO_4} + \underset{\substack{\text{Acetate of}\\\text{sodium.}}}{2NaC_2H_3O_2}$$

$$= \underset{\substack{\text{Ferrous}\\\text{phosphate.}}}{Fe_32PO_4} + \underset{\substack{\text{Sulphate of}\\\text{sodium.}}}{3Na_2SO_4} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2}$$

Officially, solutions of 3 ounces of sulphate of iron in a quart of water and 2½ ounces of phosphate and 1 of acetate of sodium in another quart of water, are well mixed, filtered, the precipitate well washed, and, to prevent oxidation as much as possible, dried at a temperature not exceeding 120° F. These proportions will be found to accord with the molecular weights of the crystalline salts, multiplied as indicated in the foregoing equation. $3(FeSO_4,7H_2O) = 834$; $2(Na_2HPO_4,12H_2O) = 716$; $2(NaC_2H_3O_2,3H_2O) = 272$.

The above reaction also occurs in making *Syrupus Ferri Phosphatis*, B. P. The precipitate should be well washed, or red ferric acetate may be developed after a time.

The use of acetate of sodium is to insure the absence of free sulphuric acid in the solution—sulphate of sodium being formed together with acetic acid. Sulphuric acid is a powerful solvent of ferrous phosphate; acetic acid is only a weak solvent. It is impossible to prevent the separation of sulphuric acid if only ferrous sulphate and phosphate of sodium be employed. The solvent action of the sulphuric acid for the ferrous phosphate is still better prevented by the use of excess of the phosphate of sodium (Price), sodium sulphate, and doubtless monosodium phosphate (NaH_2PO_4,H_2O) resulting. Ferrous phosphate is white, but soon oxidizes and becomes slate-blue.

Sulphide of Iron. Ferrous Sulphide.

Fifth Synthetical Reaction.—In a gas- or spirit-flame strongly heat sulphur with about twice its weight of iron filings in a test-tube (or in an earthen crucible in a furnace); ferrous sulphide (FeS) is formed. When cold, add water to a small portion, and then a few drops of sulphuric acid; sulphuretted hydrogen gas (H_2S), known by its odor, is evolved.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Sticks of sulphur pressed against a white-hot bar of cast iron give a pure form of ferrous sulphide. The liquid sulphide thus formed is allowed to drop into a vessel of water. Or melted sulphur may be poured into a crucible full of red-hot iron nails, when a quantity of fluid ferrous sulphide is at once formed and may be poured out on to a slab.

Green Iodide of Iron. Ferrous Iodide.

Sixth Synthetical Reaction.—Place a piece of iodine, about the size of a pea, in a test-tube with a small quantity of water, and add a few iron filings, small nails, or iron wire. On gently warming, or merely shaking if longer time be allowed, the iodine disappears, and, on filtering, a clear light-green solution of iodide of iron (FeI_2) is obtained.

The official Ferri Iodidum, B. P., is formed by gently warming a mixture of 3 parts of iodine, 1½ of fine iron wire, and 12 of distilled water in an iron vessel. When combination is nearly complete (as shown by indications of a sea-green tint), boil for a short time until the whiteness of the froth proves that the iodine has entirely disappeared. The solution is then filtered and evaporated in a clean bright iron saucepan, ladle, or dish until a drop taken out on the end of an iron wire stirrer solidifies on cooling. The liquid is poured out on a clean smooth slab, broken up and preserved in a glass-stoppered bottle. Solid iodide of iron has a crystalline fracture, is "green with a tinge of brown; inodorous, deliquescent, and almost entirely soluble in water, forming a slightly green solution which gradually deposits a colored sediment and acquires a red color."

The solid iodide contains about 18 per cent. of water of crystallization, and a little oxide of iron. It is deliquescent and liable to absorb oxygen from the air, with formation of insoluble ferric oxyiodide or hydrato-iodide. Iodide of iron thus spoiled may be purified by re-solution in water, addition of a little more iodine and some iron, warming, filtering, and evaporating as before.

Ferrous bromide ($FeBr_2$), occasionally used in medicine, could be made, as might be expected, in the same way as the iodide. *Syrupus Ferri Bromidi*, U. S. P., contains 10 per cent. of ferrous bromide.

Ferri Iodidum Saccharatum, U. S. P., is made by mixing 6 parts of iron, 17 of iodine, and 20 of water, shaking until reaction ceases, filtering into 40 parts of sugar of milk, evaporating to dryness with frequent stirring, and mixing the product in a mortar with 20 additional parts of sugar of milk. It is a grayish or yellowish-white hygroscopic powder.

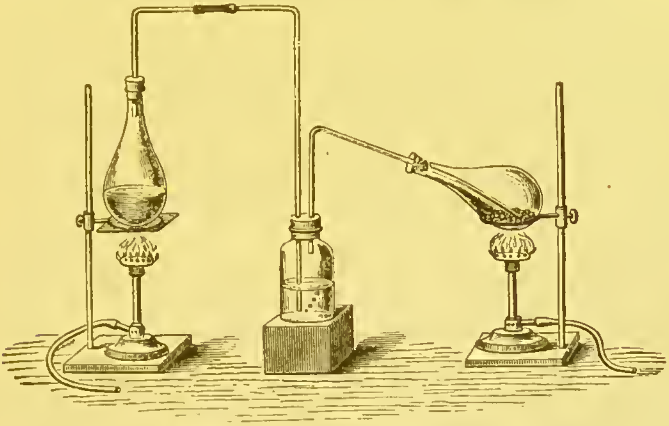
Syrupus Ferri Iodidum, U. S. P., contains 10 per cent. of the iodide.

FERRIC SALTS.

Anhydrous Perchloride of Iron. Ferric Chloride.

Seventh Synthetical Reaction.—Pass chlorine (generated as usual from black oxide of manganese and hydrochloric acid in a flask) through sulphuric acid contained in a small bottle, and thence by the ordinary narrow glass tubing quite to the bottom of a test-tube containing twenty or thirty small iron tacks (or a Florence flask containing 2 or 3 ounces of iron tacks), the latter kept hot by a gas-flame; the higher chloride of iron, ferric chloride, or the perchloride* of iron (Fe_2Cl_6), is formed, and condenses in the upper part of the tube or flask as a mass of small dark, iridescent crystals. When a tolerably thick crust of the salt is formed, break off the part of the glass containing it, being careful that the remaining corroded tacks are excluded, and place it in ten or twenty times its weight of water; the resulting solution, poured off from any pieces of glass, is a pure neutral solution of hydrous ferric chloride, and will be serviceable in performing analytical reactions.

Fig. 31.



Preparation of Anhydrous Ferric Chloride.

Precaution.—The above experiment must be conducted in the open air, or in a cupboard having a draught outwards.

Anhydrous Ferrous Chloride.—In breaking up the tube, small scales of a light buff color will be observed adhering to the nails; they are crystals of ferrous chloride ($FeCl_2$).

Note.—Solution of ferric chloride evolves some hydrochloric acid on boiling, while a darker colored solution of ferric oxychloride remains.

Green Chloride of Iron. Hydrous Ferrous Chloride. Solution of Hydrous Ferric Chloride.

Eighth Synthetical Reaction.—Dissolve iron tacks, in a test-tube, in hydrochloric acid; hydrogen escapes, and the solution on cooling, or on evaporation and cooling, deposits *crystallized ferrous chloride* ($FeCl_2$), associated with four molecules of water ($4H_2O$) of crystallization ($FeCl_2,4H_2O$).

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* The prefixes *per* and *hyper* used here and elsewhere are from ὑπέρ, *hyper*, over and above, and simply mean "the highest" of several. Thus perchloride, the highest *chloride*.

Through a portion of the solution of ferrous chloride pass chlorine gas; the ferrous chloride becomes *ferric chloride.*

The excess of chlorine dissolved by the liquid in this experiment may be removed by ebullition; but the ferric chloride is slightly decomposed at the same time, for the reason just stated. The free chlorine may also be carried off by passing a current of air through the liquid for some time.

Hydrous Ferric Chloride (another process).

Ninth Synthetical Reaction.—To another portion of the solution of ferrous chloride, in a test-tube, add a little more hydrochloric acid; heat the liquid, and continue to drop in nitric acid until the black color it first produces disappears; the resulting reddish-brown liquid is also solution of ferric chloride.

$$\underset{\substack{\text{Ferrous}\\\text{chloride.}}}{6FeCl_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Ferric}\\\text{chloride.}}}{3Fe_2Cl_6} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

The black substance is a compound of nitric oxide gas (NO) with a portion of the ferrous salt; it is decomposed by heat.

This is the process for producing the *Liquor Ferri Chloridi*, U. S. P., definite weights of materials being employed and the solution of ferrous chloride being poured slowly into the nitric acid. The sp. gr. of the *Liquor* is 1.405. It contains some free hydrochloric acid. Percentage of anhydrous chloride, 37.8.

35 parts of this solution and 65 of alcohol form the *Tinctura Ferri Chloridi*, U. S. P.

Note.—The spirit in the tincture is unnecessary, useless, and deleterious; for it acts neither as a special solvent nor as a preservative, the offices usually performed by alcohol (*Tincturæ et Succi*, B. P. and U. S. P.), but, unless the liquid contain excess of acid, decomposes the ferric chloride and causes the formation of an insoluble oxychloride of iron. Even if the tincture be acid, it slowly loses color, ferrous chloride and chlorinated ethereal bodies being formed. A *Liquor*, of similar strength, is doubtless destined to displace the tincture altogether.

A strong solution of ferric chloride, on standing, yields a mass of yellow crystals (*Ferri Chloridum*, U. S. P.) containing $Fe_2Cl_6,12H_2O$, or, rarely, red crystals having the formula $Fe_2Cl_6,5H_2O$.

Persulphate of Iron. Ferric Sulphate.

Tenth Synthetical Reaction.—Dissolve ferrous sulphate with about a fifth of its weight of sulphuric acid in water in an evaporating-dish, heat the mixture and drop in nitric acid until the black color it first produces disappears; the resulting liquid, when made of a certain prescribed strength, is the solution of ferric sulphate, or higher sulphate, "Solution of Persulphate of Iron" of the Pharmacopœia, a heavy dark-red liquid, sp. gr. 1.320 (*Liquor Ferri Tersulphatis*, U. S. P.). *Liquor Ferri Subsulphatis*, U. S. P. (Monsel's Solution), is a similar fluid, made with less acids, containing, therefore, ferric oxysulphate, Fe_4O5SO_4 (sp. gr. 1.555).

$$\underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{6FeSO_4} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{3HSO_4} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{2HNO_3} = \underset{\substack{\text{Ferric}\\ \text{sulphate.}}}{3(Fe_23SO_4)} + \underset{\substack{\text{Nitric}\\ \text{oxide.}}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

The black color, as in the previous reaction, is due to a compound of ferrous salt with nitric oxide ($2FeSO_4 + NO$).

Note.—In all the reactions in which iron passes from ferrous to ferric condition the element assumes different properties, the chief one being an alteration from bivalent to trivalent activity.

The official "Solution of Normal Ferric Sulphate" or Tersulphate, just mentioned, is made by heating a mixture of 15 parts of sulphuric acid, 11 of nitric, and 50 of water, and adding 80 of ferrous sulphate (about one-fourth at a time); then dropping in more nitric acid until red fumes cease to be produced and heating until the fluid has a reddish-brown color and is free from nitrous odor. Water is added to make 200 parts. It contains 28.7 per cent. of anhydrous ferric sulphate.

Acetate of Iron. Ferric Acetate.

Eleventh Synthetical Reaction.—To a strong solution of ferric sulphate (from which free nitric acid has been removed by evaporating to dryness and redissolving in water) add an *alcoholic* solution of acetate of potassium ($KC_2H_3O_2$), and well shake the mixture; a crystalline precipitate of sulphate of potassium (K_2SO_4) falls, and ferric acetate ($Fe_26C_2H_3O_2$) remains in solution, forming, when filtered and of definite strength, the *Tinctura Ferri Acetatis*, B. P. The preparation is unstable.

$$\underset{\substack{\text{Ferric}\\ \text{sulphate.}}}{Fe_23SO_4} + \underset{\substack{\text{Acetate of}\\ \text{potassium.}}}{6KC_2H_3O_2} = \underset{\substack{\text{Sulphate of}\\ \text{potassium.}}}{3K_2SO_4} + \underset{\substack{\text{Ferric}\\ \text{acetate.}}}{Fe_26C_2H_3O_2}$$

The official proportions are 2½ fluidounces of "Solution of Persulphate of Iron" with 8 fluidounces of rectified spirit, mixed with a solution of 2 ounces of acetate of potassium in 10 fluidounces of spirit, the whole well shaken frequently during an hour, filtered, and the precipitated sulphate of potassium washed by pouring on spirit until the filtrate measures 1 pint. A solution four times this strength, made from ferric hydrate and glacial acetic acid, is stable: it is diluted with spirit as wanted (J. Deane and T. Jeaffreson).

The Solution of Acetate of Iron (*Liquor Ferri Acetatis*, U. S. P.) is an aqueous solution of ferric acetate, containing 33 per cent. of $Fe_26C_2H_3O_2$. It is made by dissolving the ferric hydrate prepared from a known quantity of ferric sulphate in a definite weight of acetic acid. Sp. gr. 1.160. 50 parts of this solution, 30 of alcohol and 20 of acetic ether form the *Tinctura Ferri Acetatis*, U. S. P.

Perhydrate of Iron. Ferric Hydrate.

Twelfth Synthetical Reaction.—Pour a portion of the solution of ferric sulphate into excess of solution of ammonia; moist ferric hydrate is precipitated (*Ferri Oxidum Hydratum*, U. S. P.).

$$\underset{\text{Ferric sulphate.}}{Fe_2 3SO_4} + \underset{\text{Ammonia.}}{6AmHO} = \underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Sulphate of ammonium.}}{3Am_2SO_4}$$

Either of the other alkalies (potash or soda) will produce a similar reaction; soda is cheapest, ammonia most convenient.

Ferric hydrate is an antidote to arsenic if administered directly the poison has been taken.

It converts the soluble arsenic (As_2O_3) into insoluble ferrous arseniate:—

$$2(Fe_2 6HO) + As_2O_3 = Fe_3 2AsO_4 + 5H_2O + Fe2HO.$$

Dried ferric hydrate (having become an oxyhydrate—$Fe_4O_4 4HO$) has less action on arsenic. Even the moist, recently prepared hydrate ($Fe_2 6HO$) loses much of this power as soon as it has become converted into an oxyhydrate ($Fe_4O_3 6HO$), a change which occurs though the hydrate be kept under water (W. Procter, Jr.). According to T. and H. Smith this decomposition occurs gradually, but in an increasing ratio; so that after four months the power of the moist mass is reduced to one-half and after five months to one-fourth. Now mere loss of water is not usually followed by any alteration of the essential chemical properties of a compound. It would seem, therefore, that ferric hydrate (two molecules) ($Fe_4 12HO$) probably suffers, on standing, actual decomposition into oxyhydrate ($Fe_4O_3 6HO$) and water ($3H_2O$), and does not merely lose water already existing in it as water. Ferric hydrate is also far more readily soluble in hydrochloric acid, tartaric acid, citric acid, and acid tartrate of potassium, than ferric oxyhydrate. Any formula exhibiting ferric hydrate ($Fe_2 6HO$) as a combination of ferric oxide and water ($Fe_2O_3,3H_2O$) is, apparently, for these and other reasons, incorrect.

Ferri Oxidum Hydratum cum Magnesia.—As a more trustworthy arsenical antidote, a mixture of solution of ferric sulphate and magnesia is recommended in the United States Pharmacopœia. Bottles containing (*a*) 100 parts of the official solution of ferric sulphate mixed with twice its weight of water, and (*b*) 15 parts of magnesia well mixed and diluted with water, are to be kept on hand ready for immediate use. Their contents are simply mixed, shaken together, and administered to the patient.

$$\underset{\text{Ferric sulphate.}}{Fe_2 3SO_4} + \underset{\text{Magnesia.}}{3MgO} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Sulphate of magnesium.}}{3MgSO_4} + \underset{\text{Ferric hydrate.}}{Fe_2 6HO}$$

Peroxyhydrate of Iron. Ferric Peroxyhydrate.

Collect the precipitate on a filter, wash, and dry on a plate over hot water; ferric oxyhydrate (*Ferri Peroxidum Hydratum*,

B. P.) (Fe_2O_22HO) remains. When rubbed to powder it is fit for use in medicine.

$$Fe_26HO = Fe_2O_22HO + 2H_2O.$$

This oxhydrate further decomposes when heated to low redness, ferric oxide (Fe_2O_3) remaining.

$$Fe_2O_22HO = Fe_2O_3 + H_2O.$$

Peroxide of Iron. Ferric Oxide.

The six univalent atoms of the HO, the characteristic elements of all hydrates, are thus, by two successive steps, split up into water and oxygen. But between the hydrate and oxide there obviously may be another oxyhydrate, in which only 2HO is displaced by O'', and such a compound is well known; it is a variety of brown iron ore. The other oxyhydrate, Fe_2O_22HO, is also native (needle iron ore), as well as being the *Ferri Peroxidum Hydratum*, B. P.

"Ferri Peroxidum Humidum"	$Fe'''_2 \quad 6HO$
A variety of brown iron ore	$Fe'''_2O''\,4HO$
"Ferri Peroxidum Hydratum" (needle ore) . .	$Fe'''_2O''_22HO$
Ferric oxide	$Fe'''_2O''_3$

The moist ferric hydrate, as already stated, when kept for some months, even under water, loses the elements of water, and is converted into an oxyhydrate having the formula $Fe_4H_6O_9$ (limonite or brown hæmatite), which is either a compound of the above oxyhydrates (Fe_2O4HO) + (Fe_2O_22HO), or is a definite intermediate oxyhydrate (Fe_4O_36HO).

By ebullition with water for seven or eight hours, ferric hydrate is decomposed into water and an oxyhydrate having the formula $Fe_4H_2O_7$ (Saint Giles), which is either a mixture of the official oxyhydrate (Fe_2O_22HO) with ferric oxide (Fe_2O_3), or a definite intermediate body (Fe_4O_52HO). The relation of these bodies to each other will be apparent from the following Table, in which, for convenience, the formulæ of ferric hydrate and oxide are doubled:—

Ferric hydrate (B. P.) (as stalactite)	$Fe_4 \quad 12HO$
Kilbride mineral (?)	Fe_4O10HO
Brown iron ore (Huttenrode and Raschau) . .	$Fe_4O_2\,8HO$
Old, or frozen, ferric hydrate (limonite) . . .	$Fe_4O_3\,6HO$
Ferric oxyhydrate (B. P.) (göthite)	$Fe_4O_4\,4HO$
Boiled ferric hydrate (turgite)	$Fe_4O_5\,2HO$
Ferric oxide (red hæmatite)	Fe_4O_6

A ferric oxycarbhydrate (Fe_4OCO_38HO) has been obtained by Rother.

The English official ferric oxyhydrate (Fe_2O_22HO), termed in the British Pharmacopœia *Hydrated Peroxide of Iron*, under the assumption that it is a compound of ferric oxide and water (Fe_2O_3,-H_2O), was formerly made by mixing solutions of ferrous sulphate and carbonate of sodium and exposing the resulting ferrous carbonate to the air until it was nearly all converted into ferric oxyhydrate; hence its old names, still sometimes seen on old bottles, of *Ferri Carbonas* and *Ferri Subcarbonas*.

Ferric Oxide (another process).

Thirteenth Synthetical Reaction.—Roast a crystal or two of ferrous sulphate in a small crucible until fumes cease to be evolved; the residue is a variety of ferric oxide (Fe_2O_3) or peroxide of iron, known in trade as *red oxide of iron*, *colcothar*, *crocus*, *rouge* (mineral), or *Venetian red*. It has sometimes been used in pharmacy in mistake for the official oxyhydrates (*vide* 12th Synthet. Reac.), from which it differs not only in composition, but in the important respect of being almost insoluble in acids.

The Scale Compounds of Iron.

Fourteenth Synthetical Reaction.—Repeat the twelfth reaction, introducing a little solution of citric or tartaric acid, or acid tartrate of potassium, before adding to the alkali (soda, potash, or ammonia), and notice that now no precipitation of ferric hydrate occurs. This experiment serves to illustrate, not the manufacture of a scale compound, but the chemistry of the manufacture. The effect is due to the formation of double compounds, termed Ammonio-Citrate, Potassio-Citrate, Ammonio-Tartrate, Potassio-Tartrate, and similar Sodium compounds of Iron, which remain in solution along with the secondary product—sulphate of the alkali metal. Such ferric compounds, made with certain prescribed proportions of recently prepared ferric hydrate (from which all alkaline sulphate has been washed), and the respective acids (tartaric or citric) or acid salts (acid tartrate of potassium), etc., and the solutions evaporated to a syrupy consistence, and spread on flat plates till dry, form the scale preparations known as *Ferri et Ammonii Citras*, U. S. P., *Ferri Citras*, U. S. P. (also *Liquor Ferri Citratis*, U. S. P.), *Ferri et Ammonii Tartras*, U. S. P., and *Ferri Potassio-tartras*, or rather *Ferrum Tartaratum*, B. P., *Ferri et Potassii Tartras*, U. S. P. A mixture of citrate of iron and ammonium with citrate of strychnine yields, on evaporation, *Ferri et Strychninæ Citras*, U. S. P. A mixture of ferric citrate with citrate of ammonium and citrate of quinine yields, by similar treatment, the well-known scales of *Ferri et Quininæ Citras*, U. S. P.

Specimens of these substances may be prepared by attending to the following details. It is essential, first, that the ferric hydrate be thoroughly washed, or an insoluble oxysulphate will be formed; second, that the ferric hydrate be rapidly washed, or an insoluble ferric oxyhydrate will be produced; thirdly, that the whole operation be conducted quickly, or reduction to green ferrous salt will occur; fourthly, that the solutions of the salts be not evaporated at a higher temperature than that stated, or decomposition will take place; and fifthly, that the full quantities of ferric hydrate be employed.

In the pharmacopœial processes for the scale compounds, the ferric hydrate is in each case freshly made from solution of ferric sulphate by precipitation with solution of ammonia,

$$\underset{\substack{\text{Ferric}\\\text{sulphate.}}}{Fe_2 3SO_4} + \underset{\substack{\text{Hydrate of}\\\text{ammonium.}}}{6AmHO} = \underset{\substack{\text{Ferric}\\\text{hydrate.}}}{Fe_2 6HO} + \underset{\substack{\text{Sulphate of}\\\text{ammonium.}}}{3Am_2SO_4}$$

the solution of ferric sulphate being made of a definite strength (see p. 146) from a known weight of ferrous sulphate. The reason for adopting this course is that ferric hydrate is unstable and cannot be weighed, because it cannot be dried without decomposing and becoming insoluble, as explained under the 12th reaction.

Ferri Citras, U. S. P., and *Ferri et Ammonii Citras*, U. S. P.—Ferric hydrate is dissolved in solution of citric acid, and the whole evaporated to dryness without or with ammonia.

To prepare the ferric hydrate, dilute 105 parts of official solution of ferric sulphate with water; pour this into water containing excess of solution of ammonia. (If the opposite course were adopted, the alkaline liquid poured into the ferric solution, the precipitate would contain ferric oxysulphate, or hydrato-sulphate, which interferes with the brilliancy of the scales.) Thoroughly stir the mixture (it will smell strongly of ammonia, if enough of the latter has been added), allow the precipitate to subside, pour away the supernatant liquid, add more water, and repeat the washing until a little of the liquid tested for by-product (sulphate of ammonium) by solution of chloride or nitrate of barium ceases to give a white precipitate (sulphate of barium). Collect the ferric hydrate on a filter, drain, and place in it, while still moist, 30 parts of citric acid, in an evaporating-basin, over a water-bath; stir frequently, until the hydrate has dissolved. Filter, and either evaporate until the liquid weighs 100 parts (*Liquor Ferri Citratis*, U. S. P., sp. gr. 1.260; strength, 35.5 per cent. of $Fe_2 2C_6H_5O_7$) or evaporate to a syrup at 60° C. and spread on glass plates to dry (*Ferri Citras*, U. S. P., $Fe_2 2C_6H_5O_7,6H_2O$), or to 3 parts of the *Liquor* add 1 of ammonia-water and evaporate to form scales (*Ferri et Ammonii Citras*, U. S. P.).

Ferri et Quininæ Citras, U. S. P., is made by dissolving 12 parts of pure quinine (dried at 100° C.) and 88 parts of citrate of iron in water, evaporating and scaling. *Liquor Ferri et Quininæ Citratis*, U. S. P., contains citrate of iron and ammonium and citrate of quinine.

Ferri et Strychninæ Citras, U. S. P., is prepared by mixing one part of strychnine and one of citric acid with a solution containing 98 parts of citrate of iron and ammonium, evaporating the mixture at a temperature not exceeding 60° C. or 140° F. to a syrupy consistence, and scaling in the usual way by spreading it upon plates of glass.

Ferri et Potassii Tartras, U. S. P.—Ferric hydrate is dissolved in solution of acid tartrate of potassium with a little ammonia, and the whole evaporated to dryness.

The ferric hydrate obtainable from twelve parts of the official solution of ferric sulphate by the action of ammonia, in the manner detailed in the previous paragraphs, is mixed (in a mortar), while still moist but well drained, with four parts of acid tartrate of potassium. The whole is then heated in a dish over a water-bath to a temperature not exceeding 140° F., and the mixture kept warm until nothing more will dissolve; a little ammonia added and the clear fluid evaporated at a temperature not exceeding 140° F. (greater heat causes decomposition), and, when the mixture has the consistence of syrup, spread on panes of glass and allowed to dry (in any warm and light place shown by a thermometer to be not hotter than 140° F.). The dry salt is then obtained in flakes. It should be kept in well-closed bottles.

Ferri et Ammonii Tartras, U. S. P., is made by saturating solution of acid tartrate of ammonium with ferric hydrate, evaporating, and scaling. The acid tartrate is prepared by exactly neutralizing half of any quantity of tartaric acid by carbonate of ammonium, and then adding the other half.

The foregoing are the only official scale preparations of iron. Many others of similar character might be formed. The *Citrate* dissolves slowly in cold but readily in warm water. None crystallize or give other indications of definite chemical composition. Their properties are only constant so long as they are made with unvarying proportions of constituents. Want of chemical compactness, the loose state in which the iron is combined, precludes their recognition as well-defined chemical compounds, yet possibly enables them to be more readily assimilated as medicines than some of the more definite ferrous and ferric salts.

A definite *ferrous tartrate* ($FeC_4H_4O_6$) and *ferrous citrate* ($FeHC_6H_5O_7,H_2O$) have been obtained by reaction of iron and acid in hot water. They occur as white masses of microscopic crystals. A *sodio-ferrous citrate* ($FeNaC_6H_5O_7$) and *hydrato-citrate* ($FeNa_2HOC_6H_5O_7$) may be obtained in scales (Rother).

Ferric phosphate (Fe_22PO_4), when freshly precipitated, is soluble in solution of citrates of the alkali-metals, and the mixture, on evaporation on glass plates, yields scales. The official (U. S. P.) *Ferri Phosphas* is to be made by adding 6 parts of phosphate of sodium to an aqueous solution of 5 parts of citrate of iron, evaporating and scaling. It is a mixture of ferric phosphate and citrate of sodium.

Wine of Iron, or "Steel" wine (*Vinum Ferri*, B. P.), made by digesting iron wire in sherry wine, probably contains tartrate of potassium and iron and other iron salts, formed by action of the metal on the acid tartrate of potassium and tartaric, citric, malic, and acetic acid present in the wine. *Vinum Ferri Citratis*, U. S. P., contains ammonio-citrate of iron; *Vinum Ferri Amarum*, U. S. P., contains citrate of iron and quinine.

Black Hydrate of Iron. Ferroso-ferric Hydrate.

Ferri Oxidum Magneticum, B. P.

Fifteenth Synthetical Reaction.—To two-thirds of a small quantity of a solution of ferrous sulphate add a little sulphuric acid; warm, and gradually add nitric acid, as described in the tenth reaction, care being taken not to allow one drop more nitric acid than necessary to fall into the test-tube. Add the other third of ferrous sulphate, shake, and pour the liquid into excess of an alkali; black (at first brown) hydrate of iron, or ferroso-ferric hydrate ($Fe_38HO = Fe2HO,Fe_26HO$), is produced.

$$\underset{\text{Ferric sulphate.}}{Fe_23SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Soda.}}{8NaHO} = \underset{\text{Blk. Hydrate of iron.}}{Fe_38HO} + \underset{\text{Sulphate of sodium.}}{4Na_2SO_4}$$

It is so readily attracted by a magnet, even when moist, as to collect round the poles when the instrument is immersed in the supernatant liquid. Hence the B. P. name, *Ferri Oxidum Magneticum.*

In this process the nitric acid oxidizes the hydrogen of the sulphuric acid, the sulphuric radical uniting with the ferrous sulphate, the iron of which is at the same time altered from the ferrous to the ferric condition, ferric sulphate being formed. If too much nitric acid be employed, the second portion of ferrous sulphate will also be converted into ferric salt, and the solution, on the addition of alkali, yield only red ferric hydrate. This result may be avoided by evaporating the solution of ferric sulphate nearly to dryness, thus boiling off excess of nitric acid, or by pouring first the ferric and then the ferrous liquid into the alkali and thoroughly stirring the mixture; any nitric acid is then neutralized and rendered incapable of oxidizing the ferrous sulphate subsequently added.

Black hydrate of iron is decomposed by heat, yielding, in a closed vessel, oxyhydrates, and, finally, black oxide of iron or ferroso-ferric oxide. Heated in the air it absorbs oxygen and gives ferric oxide. The black *forge-scales* which collect near the blacksmith's anvil have the composition of ferroso-ferric oxide: the black magma formed on exposing a mixture of iron and water to the air is ferroso-ferric hydrate; but these varieties are apt to contain particles of metal, and hence give hydrogen gas when dissolved in acids—a character which distinguishes them from the official preparation.

If a dried specimen of the black hydrate of iron be required, the mixture should be well boiled and then set aside for an hour or two to favor aggregation of the particles, the mixture filtered, and the precipitate washed until the washings contain no trace of sulphate (that is, until they no longer yield a white precipitate with chloride of barium). Black hydrate of iron absorbs oxygen even at the temperature of the water-bath; it should consequently be dried at 120°, a temperature at which only slight oxidation occurs.

Pernitrate of Iron. Ferric Nitrate.

Sixteenth Synthetical Reaction.—Place a few iron tacks in dilute nitric acid and set aside; solution of ferric nitrate, or pernitrate of iron, is formed ($Fe_2 6NO_3$).

$$\underset{\text{Iron.}}{Fe_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Ferric nitrate.}}{Fe_2 6NO_3} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitric oxide.}}{2NO}$$

Precipitate ferric hydrate from solution of ferric sulphate, wash, and dissolve it in nitric acid.

$$\underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Nitric acid.}}{6HNO_3} = \underset{\text{Ferric nitrate.}}{Fe_2 6NO_3} + \underset{\text{Water.}}{6H_2O}$$

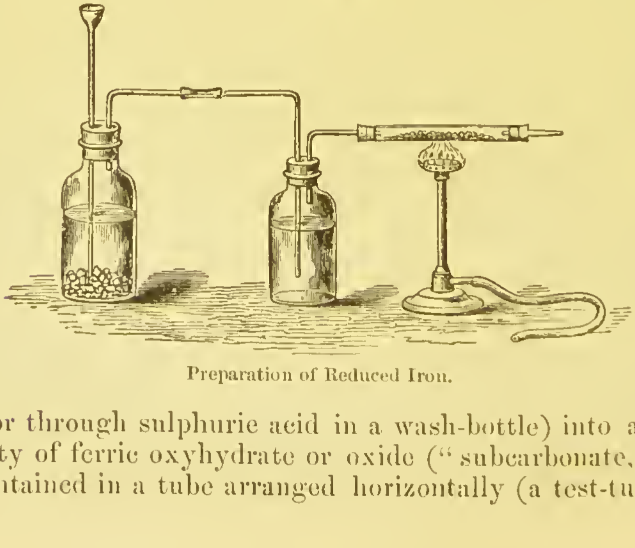
The latter is the official method for preparing *Liquor Ferri Nitratis*, U. S. P., definite quantities of solution of ferric sulphate and of nitric acid being employed. Sp. gr. 1.050. Strength, about 6 per cent. of anhydrous nitrate.

Ferric nitrate and ferric acetate unite to form various aceto-nitrates, amongst which is one having the formula $Fe_2 4C_2H_3O_2, NO_3, HO, 4H_2O$, crystallizing in hard, shining, brownish-red prisms.

Reduced Iron.

Seventeenth Synthetical Reaction.—Pass hydrogen gas (dried by passing over pieces of chloride of calcium contained in a tube, or through sulphuric acid in a wash-bottle) into a small quantity of ferric oxyhydrate or oxide ("subcarbonate," U. S. P.) contained in a tube arranged horizontally (a test-tube, the

Fig. 32.



Preparation of Reduced Iron.

bottom of which has been accidentally broken, answers very well), the oxide being kept hot by a gas-flame; oxygen is removed from the oxide by the hydrogen, steam escapes at the open end of the tube, and after a short time, when moisture ceases to be evolved, metallic iron, in a minute state of division, remains. (See Fig. 32.)

$$\underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Iron.}}{Fe_2} + \underset{\text{Water.}}{3H_2O}$$

While still hot throw the iron out into the air; it takes fire and falls to the ground as oxide.

If the ferric oxide is reduced in a gun-barrel heated by a strong furnace, the particles of iron aggregate to some extent, and, when cold, are only slowly oxidized in dry air. This latter form of reduced iron is *Fer réduit* or *Quevenne's Iron*, *the ferri pulvis*, or *Ferrum Reductum*, U. S. P.—"a fine grayish-black powder, strongly attracted by the magnet, and exhibiting metallic streaks when rubbed with firm pressure in a mortar."

Note I.—The spontaneous ignition of the iron in the above experiment is an illustration of the influence of minute division on chemical affinity. The action is the same as occurs whenever iron rusts, and the heat evolved and amount of oxide formed is not greater from a given quantity of iron; but the surface exposed to the action of the oxygen of the air is, in the case of this variety of reduced iron, so enormous compared with the weight of the iron, that heat cannot be conducted away sufficiently fast to prevent elevation of temperature to a point at which the whole becomes incandescent. In the slow rusting of iron escape of heat occurs, but is not observed, because spread over a length of time; in the spontaneous ignition of reduced iron the whole is evolved at one moment. The mixture of lead and carbon (lead pyrophorus) resulting when tartrate of lead is heated in a test-tube until fumes cease to be evolved, spontaneously ignites when thrown into the air, and for the same reason. Many substances, solid and liquid, if sufficiently finely divided and liable to oxidation, and especially if exposed in a warm place, become hot, and even occasionally spontaneously burst into flame. Oil on cotton-waste, powdered charcoal, coal, especially if pyritic or if very porous, or if powdered, resins in powder, and even flour, are familiar illustrations of materials liable to "heat" or even burn spontaneously.

Note II.—The student having time and opportunity for the experiment is advised to make this seventeenth reaction a roughly quantitative one, by way of realizing what has been stated (see, again, the General Principles of Chemical Philosophy, pp. 36–59) respecting the action of chemical force on definite weights only of matter. Three tubes, similar to the oxide-tube shown in the engraving, should be prepared, the second being connected to the first and the third to the second by India-rubber tubing in the usual manner. The first tube should contain pieces of chloride of calcium to absorb any traces of moisture not retained by the sulphuric acid. The second tube (the ends of the small tube being temporarily closed by small corks) should be weighed in any ordinary scales which will turn with a quarter or half of a grain, and, the weight being noted, 160 grains of dry ferric oxide should be neatly placed in the middle of the tube. (The oxide must be previously gently heated in a small crucible over a lamp to remove all traces of moisture.) The third tube should contain pieces of chloride of calcium to absorb the water produced in the reaction, and just before being connected should be weighed. The operation is now carried out. At its close, and when the middle tube is cold, the latter tube and the third tube are again weighed. The oxide-tube should weigh 48 grains less than before, and the terminal tube 54 grains more than before.

$$\underbrace{Fe_2O_3}_{112 + 48 = 160} + \underbrace{3H_2}_{6} = \underbrace{Fe_2}_{112} + \underbrace{3H_2O}_{54}$$

The operation is more quickly and easily performed if one-half or one-quarter of the weight of oxide be taken; in that case one-half or one-quarter of the weight of iron and of water will be obtained. Indeed any weight of oxide may be employed; the amount of iron and water resulting will be *always exactly proportionate* to the weights just mentioned. Thus 16 parts of oxide yield 11.2 of iron and 5.4 of water. Iron, hydrogen, and oxygen always combine in proportions of 56, 1, and 16 respectively; hence our justification for agreeing that the symbol Fe shall stand for 56, more exactly 55.9, parts by weight of iron, H for 1 part by weight of hydrogen, and O for 16 parts by weight of oxygen.

Ferric Pyrophosphate.

Eighteenth Synthetical Reaction.—To solution of pyrophosphate of sodium add solution of ferric sulphate; a yellowish-white precipitate of ferric pyrophosphate ($Fe_43P_2O_7,9H_2O$) separates.

The official (U. S. P.) *Ferri Pyrophosphas* is to be made by adding 10 parts of pyrophosphate of sodium to an aqueous solution of 9 parts of citrate of iron, evaporating and scaling. The apple-green product is a mixture of ferric pyrophosphate and citrate of sodium.

(*b*) *Reactions having Analytical Interest* (*Tests*).

(The iron occurring as a ferrous salt.)

First Analytical Reaction.—Pass sulphuretted hydrogen (H_2S) through a solution of a ferrous salt (*e. g.*, ferrous sulphate) slightly acidulated by hydrochloric acid; no precipitate occurs. This is a valuable negative fact, as will be evident presently.

Second Analytical Reaction.—Add sulphydrate of ammonium (NH_4HS) to solution of a ferrous salt; a black precipitate of ferrous sulphide (FeS) falls.

$$FeSO_4 + 2AmHS = FeS + Am_2SO_4 + H_2S.$$

Third Analytical Reaction.—Add solution of ferrocyanide of potassium (yellow prussiate of potash), $K_4Fe''Cy_6$, or K_4Fcy'''', to solution of a ferrous salt; a precipitate ($K_2Fe''Fe''Cy_6$, or $K_2Fe''Fcy$) falls, at first white, or bluish-gray, but rapidly becoming blue, owing to absorption of oxygen.

Fourth Analytical Reaction.—To solution of a ferrous salt add ferridcyanide of potassium (red prussiate of potash), $K_6Fe'''_2Cy_{12}$, or K_6Fdcy; a precipitate ($Fe''_3Fe'''_2Cy_{12}$, or Fe''_3Fdcy) resembling Prussian blue (Turnbull's blue) is thrown down.

Other Analytical Reactions.—The precipitates produced from ferrous solutions on the addition of alkaline carbonates, phosphates, and arseniates, as already described in the synthetical reactions of ferrous salts, are characteristic, and hence have a certain amount of analytical interest, but are inferior in this respect to the four reactions above mentioned.

Note.—Alkalies (potash, soda, or ammonia) are incomplete precipitants of ferrous salts, hence are almost useless as tests, To solution of a ferrous salt add ammonia (NH_4HO); on filtering off the whitish ferrous hydrate and testing the solution with sulphydrate of ammonium, iron will still be found. To another portion of the ferrous solution add a few drops of nitric acid and boil; this converts the ferrous into ferric salt, and now alkalies will wholly remove the iron, as already twice seen during the performance of the synthetical experiments.

In actual analysis, the separation of iron as ferric hydrate is an operation of frequent performance. This is always accomplished by the addition of alkali, and, if the iron occurs as a ferrous salt, by previous ebullition with a little nitric acid. Ferrocyanide and ferridcyanide of potassium are the reagents used in distinguishing ferrous from ferric salts.

(The iron occurring as a ferric salt.)

Fifth Analytical Reaction.—Through a ferric solution (ferric chloride, *e.g.*) pass sulphuretted hydrogen ; a white precipitate of the sulphur of the sulphuretted hydrogen falls, and the ferric is reduced to a ferrous salt, the latter remaining in solution. This reaction is of frequent occurrence in practical analysis.

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2.$$

Sixth Analytical Reaction.—Add sulphydrate of ammonium to a ferric solution ; the latter is reduced to the ferrous state, and black ferrous sulphide (FeS) is precipitated as in the second analytical reaction, sulphur being set free.

Seventh Analytical Reaction.—To a ferric solution add ferrocyanide of potassium (K_4FeCy_6, or K_4Fcy'''') ; a precipitate of Prussian blue, the common pigment, occurs ($Fe'''_43Fe''Cy_6$, or $Fe'''_4Fcy''''_3$).

Eighth Analytical Reaction.—To a ferric solution add solution of ferridcyanide of potassium ; no precipitate occurs, but the liquid is darkened to a brownish-red or to a greenish or olive hue if the salts are not quite pure.

Ninth Analytical Reaction.—This is the production of a red precipitate of ferric hydrate, on the addition of alkalies to ferric salts, and is identical with the twelfth synthetical reaction.

Note.—This reaction illustrates the conventional character of the terms synthesis and analysis. It is of equal importance to the manufacturer and the analyst, and is synthetical or analytical according to the intention with which it is performed.

Other ferric reactions have occasional analytical interest. In neutral ferric solutions the tannic acid in aqueous infusion of galls occasions a bluish-black inky precipitate, the basis of most black writing inks.——(The *Mistura Ferri Aromatica* of the British Pharmacopœia, made by digesting metallic iron in an infusion of various vegetable substances, contains tannate, or rather tannates, of iron : it is commonly known in Ireland by the name of Heberden's Ink, after the physician by whom it was first used. It contains about 1 grain of iron in 1 pint.) ——*Sulphocyanide of Potassium* (KCyS) causes the formation of ferric sulphocyanide, which is of a deep blood-red color. ——There is no ferric carbonate ; alkaline carbonates cause the precipitation of ferric hydrate, while carbonic acid gas escapes.

Note.—Cyanogen (CN, or Cy'), ferrocyanogen (FeC_6N_6, or $FeCy_6$, or simply Fcy''''), and ferridcyanogen (Fe_2Cy_{12}, or $Fdcy^{VI}$), are radicals which play the part of non-metallic elements, just as ammonium in its chemical relations resembles the metallic elements. They will be again referred to.

Memorandum.—The reader must on no account omit to write out equations or diagrams expressive of each of the reactions of iron, analytical as well as synthetical. It is presumed that this has already been done immediately after each reaction has been performed.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING **ONE** OF THE METALS, ZINC, ALUMINIUM, IRON.

Add solution of ammonia gradually :

A dirty-green precipitate indicates iron in the state of a ferrous salt.

A red precipitate indicates iron in the state of a ferric salt.

A white precipitate, insoluble in excess, indicates the presence of an aluminium salt.

A white precipitate, soluble in excess, indicates zinc.

These results may be confirmed by the application of some of the other tests to fresh portions of the solution.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTION TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF **ONE, TWO, OR ALL THREE** OF THE METALS, ZINC, ALUMINIUM, IRON.

Boil about half a test-tubeful of the solution with a few drops of nitric acid. This insures the conversion of ferrous into ferric salts, and enables the next reagent (ammonia) *completely* to precipitate the iron. Add excess of ammonia, and shake the mixture. Filter.

<table>
<tr><td colspan="2">Precipitate
Al Fe.*
Dissolve in HCl, add excess of KHO, stir, filter.</td><td rowspan="2">Filtrate
Zn.
Test by AmHS (white ppt.).</td></tr>
<tr><td>Ppt.
Fe
(red ppt.).</td><td>Filtrate
Al.
Make slightly acid by HCl, and add excess of AmHO† (white ppt.).</td></tr>
</table>

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* The aluminium precipitate (Al_26HO) is white, the iron (Fe_26HO) red. If the precipitate is red, iron must be and aluminium may be present; if white, iron is absent, and further operations on the ppt. are unnecessary. This precipitate (Al_26HO and Fe_26HO) may also, if sufficient is at disposal, be analyzed by simply well shaking a washed portion in a tube with solution of potash or soda; the hydrate of iron is not thereby affected, while the hydrate of aluminium is dissolved, and may be detected in the clear decanted fluid by neutralizing all alkali by a little excess of acid, and then adding excess of ammonia.

† Alumina, when in small quantity, is sometimes prevented from

Note I.—If iron is present, portions of the original solution must be tested by ferridcyanide of potassium for ferrous, and by ferrocyanide for ferric salts; dark-blue precipitates with both indicate both salts.

Note II.—If no ferrous salt is present, ebullition with nitric acid is unnecessary. It is, perhaps, therefore advisable always to determine this point by *previously* testing a little of the original solution with ferridcyanide; if no blue precipitate occurs, the nitric acid treatment may be omitted.

CHART FOR ALL METALS HITHERTO CONSIDERED.

The following Table (*vide* p. 161) is perhaps the best, but not the only, adaptation of the ordinary reactions to systematic analysis. In it the analytical scheme for the third group is added to that of the first two groups. As before, analysis is commenced by the addition of chloride of ammonium (NH_4Cl) to prevent partial precipitation of magnesium, and by ammonia (NH_4HO) to neutralize any acid. For acid destroys the group precipitant, sulphydrate of ammonium (NH_4HS), preventing its useful action, and causing a precipitation of the free sulphur it commonly contains. Any precipitate by the ammonia may be disregarded, for the sulphydrate attacks both solid and liquid.

Note.—When a test gives no reaction, absence of the body sought for may be fairly inferred. If a group-test (that is, a test which precipitates a group of substances) gives no reaction, the analyst is saved the trouble of looking for any of the members of that group.

QUESTIONS AND EXERCISES.

207. Name the chief ores of iron.

208. How is the metal obtained from the ores?

209. What is the chemical difference between cast iron, wrought iron, and steel?

210. Explain the process of welding.

211. What is the nature of chalybeate waters?

212. Illustrate by formula the difference between ferrous and ferric salts.

213. Under what different circumstances may the atom of iron be considered to exert bivalent, trivalent, and sexivalent activity?

214. Write a paragraph on the nomenclature of iron salts.

215. Give a diagram of the official process for the preparation of ferrous sulphate.

216. In what respects do Sulphate of Iron, Granulated Sulphate of Iron, and dried Sulphate of Iron differ?

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being precipitated by ammonia through the presence of organic matter derived from the filter-paper by action of the potash. In cases of doubt, therefore, before adding ammonia boil the liquid with a little nitric acid, which destroys any organic matter.

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Add AmCl; AmHO; AmHS; stir, filter.

<table>
<tr><td colspan="3">Precipitate
Fe Al Zn.
Wash, dissolve in HCl,* boil (to remove H_2S), filter (to remove S), add excess of KHO,† stir, filter.</td><td colspan="4">Filtrate
Ba Ca Mg Am Na K.
Add Am_2CO_3, boil, filter.</td></tr>
<tr><td rowspan="2">Ppt.
Fe
(test orig. sol. by K_4Fcy and K_6Fdcy).</td><td colspan="2">Filtrate
Al Zn.
Neutralize with HCl.
Add AmHO, stir, filter.</td><td colspan="2">Ppt.
Ba Ca.
Dissolve in $HC_2H_3O_2$,
Add K_2CrO_4, filter.</td><td colspan="2">Filtrate
Mg Am Na K.
Add Am_2HPO_4, stir, filter.</td></tr>
<tr><td>Ppt.
Al
(white).</td><td>Filtrate
Zn.
Add AmHS
(white ppt.).</td><td>Ppt.
Ba
(yellow).</td><td>Filtrate
Ca
Add $Am_2C_2O_4$
(white ppt.).</td><td>Ppt.
Mg
(white).</td><td>Filtrate
Am Na K.
Evap., ignite, dissolve.
Na by flame; K by $PtCl_4$: orig. sol. for Am.</td></tr>
</table>

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* Add, also, a few drops of HNO_3 if Fe be present—*i. e.*, if the ppt. be black. (*Vide* notes on pp. 157 and 160.)

† Or add excess of ammonia, filter, and test filtrate for zinc. The hydrates of iron and aluminium may then be separated by an alkali, as described in the foot-note to the previous table, p. 159.

217. How is ferrous sulphate obtained on the large scale?

218. Mention the chemical names of white, green, and blue vitriol.

219. Why does ferrous sulphate become brown by prolonged exposure to air?

220. Give a diagram showing the formation of Ferrous Carbonate.

221. Describe the action of atmospheric oxygen on ferrous carbonate. Can the effect be prevented?

222. In what order would you mix the ingredients of *Mistura Ferri Composita*, and why?

223. Write out an equation illustrative of the formation of the Phosphate of Iron.

224. Why is acetate of sodium used in the preparation of ferrous phosphate?

225. Which four compounds of iron may be formed by the direct union of their elements?

226. Give the official method for the preparation of Solution of Ferric Chloride.

227. Of what use is the spirit in Tincture of Perchloride of Iron?

228. How may Ferrous be converted into Ferric Sulphate?

229. What is the formula of Ferric Acetate? And how is it prepared for use in pharmacy?

230. Express by formulæ the difference between *Ferri Peroxidum Humidum*, B. P., and *Ferri Peroxidum Hydratum*, B. P.

231. How does Ferric Hydrate act as an antidote to arsenic?

232. What are the properties of anhydrous ferric oxide?

233. What are the general characters and mode of production of the medicinal scale preparations of iron?

234. In what state is the iron in *Vinum Ferri Amarum*, U. S. P.?

235. What other form of Wine of Iron is official?

236. Give equations illustrating the chief steps in the artificial production of the so-called Magnetic Oxide of Iron.

237. How is precipitated magnetic oxide of iron distinguished from the varieties made directly from the metal?

238. Why is magnetic oxide of iron officially directed to be dried at a temperature not exceeding 120° Fahr?

239. Give a diagram showing the formation of Ferric Nitrate.

240. Work out a sum showing how much anhydrous ferric oxide will yield, theoretically, one hundred-weight of iron. Ans. 160 lbs.

241. What are the properties of anhydrous ferric oxide?

242. Give the characteristic tests for iron, distinguishing between ferrous and ferric reactions, and illustrating each by an equation or a diagram:—

a. Sulphydrate of ammonium.
b. Ferrocyanide of potassium.
c. Ferridcyanide of potassium.
d. Caustic alkalies.
e. Sulphocyanide of potassium.

243. Describe the action of ammonia on salts of iron, aluminium, and zinc respectively.

244. What precautions must be used in testing for calcium a solution containing iron?

245. How is magnesium detected in the presence of zinc?

246. How is aluminium detected in the presence of magnesium?

247. Draw up a scheme for the analysis of an aqueous liquid containing salts of iron, barium, and potassium.

248. How may zinc, magnesium, and ammonium be consecutively removed from aqueous solution?

ARSENICUM, ANTIMONY.

These elements resemble metals in appearance and in the character of some of their compounds; but they are still more closely allied to the non-metals, especially to phosphorus and nitrogen. Their atoms are quinquivalent (As^V, Sb^V), as seen in arsenic anhydride (As_2O_5) and pentachloride of antimony ($SbCl_5$), but usually exert trivalent activity only (As^{III}, Sb^{III}), as seen in the hydrogen and other compounds (AsH_3, $AsCl_3$, $AsBr_3$, AsI_3). A few preparations of these elements are used in medicine; but all are more or less powerful poisons, and hence have considerable toxicological interest. The iodide (*Arsenii Iodidum*, U. S. P.) may be made by cautiously fusing together atomic proportions of arsenicum and iodine. It is an orange-red crystalline solid, soluble in water. The *Liquor Arsenii et Hydrargyri Iodidi*, U. S. P., or "Donovan's Solution," is made by dissolving iodide of arsenicum and red iodide of mercury in water, in the proportion of 1 per cent. of each. The old Donovan's Solution contained in each fluidounce (wine measure) the equivalents of 1 grain of white arsenic (As_2O_3), 2 grains of peroxide of mercury, and about 7 grains of iodine.

Arsenicum is an exception to the rule that the atomic weights (taken in grains, grammes, or other weight) of elements, under similar circumstances of temperature and pressure, give equal volumes of vapor, the equivalent weight (75) of arsenicum only occupying half such a volume. Hence, while the molecular weights (that is, double the atomic weights of oxygen ($O_2 = 32$), hydrogen ($H_2 = 2$), nitrogen ($N_2 = 28$), etc.) give a similar bulk of vapor at any given temperature and pressure, the double atomic weight of arsenicum ($As_2 = 150$), at the same temperature and pressure, only affords half this bulk. It would appear, therefore, that the molecule of arsenicum contains four atoms, and that its formula is As_4. As in the case of sulphur, however, arsenicum, in the state ordinarily known to us, may be abnormal, and a variety yet be found in which the molecular weight is double (instead of quadruple) the atomic weight.

From observed analogy between the two metals, the molecular constitution of antimony is probably similar to that of arsenicum.

ARSENICUM.

Symbol As. Atomic weight 74.9.

Sources.—Arsenical ores are frequently met with in nature, the commonest being the arsenio-sulphide of iron (FeSAs). This mineral is roasted in a current of air, the oxygen of which, combining with the arsenicum, forms common white arsenic (As_2O_3, possibly As_4O_6) (*Acidum Arseniosum*, U. S. P.), or arsenious oxide, which is condensed in chambers or long flues. It commonly "occurs as a heavy white powder, or in sublimed masses, which usually present a stratified appearance, caused by the existence of separate layers, differing from each other in degrees of opacity." The vitreous or amorphous arsenic is far more soluble than the crystalline variety, and in other respects they differ in properties. Such differences between the crystalline and amorphous varieties of an element or compound are not unfrequent: they have not yet been satisfactorily explained. *Realgar* (red algar) is the red native sulphide (As_2S_2), and orpiment (*auripigmentum*, the golden pigment) the yellow native sulphide (As_2S_3) of arsenicum. The iodide of arsenicum (AsI_3) may be made from its elements or (Babcock) by dissolving white arsenic in aqueous hydriodic acid and evaporating.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Reactions having Synthetical Interest.*

Alkaline Solution of Arsenic.

First Synthetical Reaction.—Boil a grain or two of powdered arsenic (As_2O_3) in water containing an equal weight of bicarbonate of potassium, and, if necessary, filter. The solution, colored with compound tincture of lavender, and containing 1 per cent. of arsenic, forms the *Liquor Potassii Arsenitis*, U. S. P. (*Fowler's Solution*).

Note.—This official solution does not generally contain arsenite of potassium; for the arsenic does not decompose the carbonate of potassium, or only after long boiling. From concentrated solutions carbonic acid gas is more quickly eliminated.

Arsenious Acids and other Arsenites.

Arsenic or *arsenious anhydride* (the so-called arsenious acid), when dissolved in water, is said to yield true arsenious acid (H_3AsO_3) —the arsenite of hydrogen.

$$\underset{\text{Arsenious anhydride.}}{As_2O_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Arsenious acid.}}{2H_3AsO_3}$$

When arsenic (As_2O_3) is dissolved in excess of solutions of potash or soda, arsenites are formed having the formulæ KH_2AsO_3 and NaH_2AsO_3. Boiled with excess of arsenic, one molecule of these salts combines with one of arsenic. The usual character of such compounds is that of oily alkaline liquids. Arsenic fused with alkaline carbonates yields pyroarseniates ($Na_4As_2O_7$ or $H_4As_2O_7$) and metallic arsenicum. Arsenites have the general formula R'_3AsO_3.

Acid Solution of Arsenic.

Second Synthetical Reaction.—Boil arsenic with dilute hydrochloric acid. Such a solution made with prescribed proportions of acid (2 per cent.) and water, and containing 1 per cent of arsenic (As_2O_3), forms the *Liquor Acidi Arseniosi*, U. S. P. (*De Valangin's Solution* contained a grain and a half per ounce.)

Note.—No decomposition occurs in this experiment. The liquid is simply a solution of arsenic in dilute hydrochloric acid. These two solutions may be preserved for analytical operations.

Mem.—The practical student should boil arsenic in water also, and thus have an acid, alkaline, and aqueous solution for analytical comparison.

Arsenicum.

Third Synthetical Reaction.—Place a grain or less of arsenic at the bottom of a narrow test-tube, cover it with about half an inch or an inch of small fragments of dry charcoal, and hold the tube, nearly horizontally, in a flame, the mouth being loosely covered by the thumb. At first let the bottom of the tube project slightly beyond the flame, so that the charcoal may become nearly red hot; then heat the bottom of the tube. The arsenic will sublime, become deoxidized by the charcoal, carbonic oxide being formed, and arsenicum be deposited in the cooler part of the tube as a dark mirror-like incrustation.

There is a characteristic odor, resembling garlic, emitted during this operation, probably due to a partially oxidized trace of arsenicum, which escapes from the tube; for arsenic does not give this odor; moreover, arsenicum being a freely oxidizable element, its vaporous particles could scarcely exist in the air in an entirely unoxidized state.

Metallic arsenicum may be obtained in large quantities by the above process if the operation be conducted in vessels of commensurate size. But performed with great care, in narrow tubes, using not charcoal alone, but *black flux* (a mixture of charcoal and carbonate of potassium obtained by heating acid tartrate of potassium in a test-tube or other closed vessel till no more fumes are evolved), the reaction has considerable analytical interest, the garlic odor and the formation of the mirror-like ring being highly characteristic of arsenicum. Compounds of mercury and antimony, however, give sublimates which may be mistaken for arsenicum.

Arsenic Acid and other Arseniates.

Fourth Synthetical Reaction.—Boil a grain or two of arsenic with a few drops of nitric acid until red fumes cease to be evolved; evaporate the solution in a small dish to dryness, to remove excess of nitric acid; dissolve the residue in water; the product is Arsen'ic acid (H_3AsO_4).

Arsenic acid, when strongly heated, loses the elements of water, and arsenic anhydride remains (As_2O_5).

Arsenic anhydride readily absorbs water and becomes arsenic acid (H_3AsO_4). Arsenic acid is reduced to arsenious by the action of sulphurous acid $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$.

Salts analogous to arsenic acid, the arseniate of hydrogen, are termed *arseniates*, and have the general formula R'_3AsO_4. The ammonium arseniate (Am_2HAsO_4) may be made by neutralizing arsenic acid with ammonia. Its solution in water forms a useful reagent. ——Arsenic acid is used as an oxidizing agent in the manufacture of the well-known dye, magenta.

Arsenite and arseniate of sodium are used in the cleansing operations of the calico-printer.

Pyroarseniate and Arseniate of Sodium.

Fifth Synthetical Reaction.—Fuse two or three grains of common white arsenic (As_2O_3) with nitrate of sodium ($NaNO_3$) and dried carbonate of sodium (Na_2CO_3) in a porcelain crucible, and dissolve the mass in water; solution of arseniate of sodium (Na_2HAsO_4) results.

$$\underset{\text{Arsenic.}}{As_2O_3} + \underset{\substack{\text{Nitrate of}\\\text{sodium.}}}{2NaNO_3} + \underset{\substack{\text{Carbonate}\\\text{of sodium.}}}{Na_2CO_3} = \underset{\substack{\text{Pyroarseniate}\\\text{of sodium.}}}{Na_4As_2O_7} + \underset{\substack{\text{Nitrous}\\\text{anhydride.}}}{N_2O_3} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

The official proportions (B. P.) are 10 of arsenic to 8½ of nitrate of sodium and 5½ of dried carbonate, each powdered, the whole well mixed, fused in a crucible at a red heat till effervescence ceases, and the liquid poured out on a slab. The product is pyroarseniate of sodium ($Na_4As_2O_7$). Dissolved in water, crystallized and dried, the salt has the formula $Na_2HAsO_4,7H_2O$ (*Sodii Arsenias*, U. S. P.).

$$Na_4As_2O_7 + 15H_2O = 2(Na_2HAsO_4,7H_2O).$$

Heated to 300° F. the crystals lose all water. A solution of 1 part of the anhydrous salt (Na_2HAsO_4) in 99 of water forms the *Liquor Sodii Arseniatis*, U. S. P. The anhydrous salt is used in this preparation because the crystallized is of somewhat uncertain composition. The fresh crystals are represented by the formula $Na_2HAsO_4,12H_2O$ (= 53.7 per cent. of water); these soon effloresce and yield a stable salt having the formula $Na_2HAsO_4.7H_2O$ (= 40.4 per cent. of water). To avoid the possible employment of a mixture of these bodies, the invariable anhydrous salt is officially used, constancy in the strength of a powerful preparation being thereby secured.

The student will find useful practice in verifying the above numbers representing the centesimal proportion of water in the two arseniates of sodium. This will readily be accomplished if what has already been stated respecting a symbol representing a number as well as a name, and the remarks concerning a molecular weight, be remembered.

The shape of each of the two varieties of arseniate of sodium ($Na_2HAsO_4,12H_2O$, and $Na_2HAsO_4,7H_2O$) is identical with that of the corresponding phosphate of sodium ($Na_2HPO_4,12H_2O$, and $Na_2HPO_4,7H_2O$); the structure of the molecule of the 12-arseniate is the same as that of the 12-phosphate, and the 7-arseniate as that of the 7-phosphate; the two former are isomorphous, the two latter are isomorphous. This is only one instance of the strong analogy of arsenicum and its compounds with phosphorus and its corresponding compounds. The preparation and characters of the next substance, arseniate of iron, will remind the learner of phosphate of iron.

Arseniate of Iron. Ferrous Arseniate.

Sixth Synthetical Reaction.—To solution of arseniate of sodium add a little acetate of sodium and then solution of ferrous sulphate; a precipitate of ferrous arseniate occurs (Fe_32AsO_4) (*Ferri Arsenias*, B. P.). On the large scale 4 parts of dried arseniate and 3 of acetate dissolved in 40 of water, mixed with 9 of sulphate in 60 of water, may be employed. The precipitate should be collected on a calico filter, washed, squeezed, and dried at a low temperature (100° F.) over a water-bath to avoid excessive oxidation.

$$\underset{\text{Arseniate of sodium.}}{2Na_2HAsO_4} + \underset{\text{Acetate of sodium.}}{2NaC_2H_3O_2} + \underset{\text{Ferrous sulphate.}}{3FeSO_4} = \underset{\text{Ferrous arseniate.}}{Fe_32AsO_4}$$

$$+ \underset{\text{Sulphate of sodium.}}{3Na_2SO_4} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2}$$

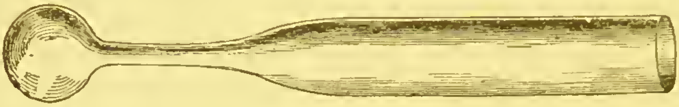
The use of the acetate of sodium is to insure the absence of free sulphuric acid in solution, sulphate of sodium being formed together with acetic acid. Sulphuric acid is a solvent of ferrous arseniate; acetic acid is not. It is impossible to prevent the separation of sulphuric acid, if only ferrous sulphate and arseniate of sodium be employed. At the instant of precipitation ferrous arseniate is white, but rapidly becomes of a green or greenish-blue color, owing to absorption of oxygen and formation of a ferroso-ferric arseniate. It is a tasteless, amorphous powder, soluble in acids.

The *Hydride* and *Sulphides* of *Arsenicum*, and the *Arsenites* and *Arseniates of Copper* and of *Silver*, are mentioned in the following analytical paragraphs:—

(*b*) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—Repeat the third synthetical reaction, operating on not more arsenic than has about the bulk of a small pin's head, and using not charcoal alone, but the *black flux* already mentioned (p. 165), or a well-made and perfectly dry mixture of charcoal and carbonate of potassium obtained by heating the bicarbonate of potassium. The tube employed should be a narrow test-tube, or, better, a tube (easily made from glass tubing) having the following (Berzelius's) form :—

Fig. 33.

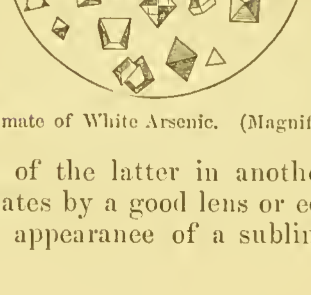


The arsenic and black flux are placed in the bulb of the tube, which is then heated in a flame; the arsenicum condenses on the constricted portion of the tube. If now the bulb be carefully fused off in a flame, the arsenicum may be chased up and down the narrower part of the tube until the air in the tube has reoxidized it to arsenious anhydride.

If the operation has been performed in a less delicate manner in an ordinary test-tube, cut or break off portions of the tube containing the sublimate of arsenicum, put them into a test-tube and heat the bottom of the latter, holding it nearly horizontally, and partially covering the mouth with the finger or thumb; the arsenicum (As_4) will absorb oxygen from the air in the tube, and the resulting arsenious anhydride (As_2O_3) be deposited on the cool part of the tube in brilliant transparent, generally imperfect, octahedral crystals.

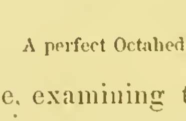
Microscopic Test.—Prove that the crystals are identical in form with those of common white arsenic, by heating a grain or less of the latter in another test-tube, examining the two sublimates by a good lens or compound microscope.

Fig. 34.



A sublimate of White Arsenic. (Magnified.)

Fig. 34*a*.



A perfect Octahedron.

The appearance of a sublimate of arsenic is peculiar and quite characteristic. The primary form of each crystal is an octahedron (*ὀκτὼ*, *okto*, eight; *ἕδρα*, *hedra*, side) (fig. 34*a*), or, rarely, a tetrahedron, and in a sublimate a few perfect octahedra are generally present. Usually, however, the crystals are modifications of octahedra, such as are shown in fig. 34—which is drawn from actual sublimates.

Second Analytical Reaction.—Place a thin piece of copper, about a quarter inch wide and half inch long, in a solution of arsenic, acidified by hydrochloric acid, and boil (nitric acid must not be present, or the copper itself will be dissolved); arsenicum is deposited on the plate in a metallic condition, an equivalent portion of copper going into solution. Pour off the supernatant liquid from the copper, wash the latter once or twice with water, dry the piece of metal by holding in the fingers and passing through a flame, and finally place it at the bottom of a clean dry narrow test-tube or a Berzelius tube; sublime as described in the last reaction, again noticing the form of the resulting crystals.

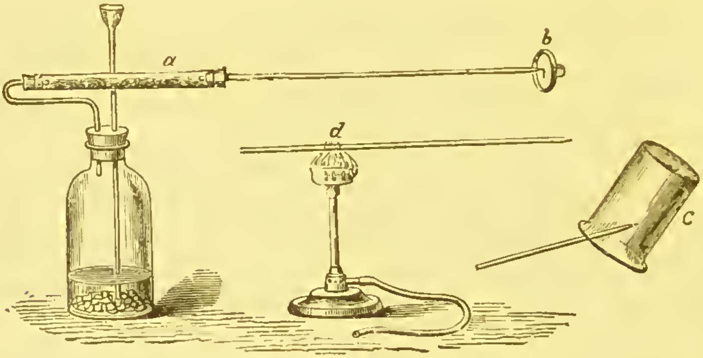
This is commonly known as Reinsch's test of arsenicum. The tube may be reserved for subsequent comparison with an antimonial sublimate (p. 185).

Note.—Copper itself frequently contains arsenicum, a fact that may not, perhaps, much trouble an operator so long as he is performing experiments in practical chemistry merely for educational purposes; but when he engages in the analysis of bodies of unknown composition, he must assure himself that neither his apparatus nor materials already contain the element for which he is in search.

The detection of arsenicum in metallic copper is best accomplished by distilling a mixture of a few grains of the sample with five or six times its weight of ferric hydrate or chloride (free from arsenicum) and excess of hydrochloric acid. The arsenicum is thus volatilized in the form of chloride of arsenicum, and may be condensed in water and detected by sulphuretted hydrogen (6th Analytical Reaction) or Reinsch's test. The ferric chloride solution is, if necessary, freed from any trace of arsenicum by evaporating once or twice to dryness with excess of hydrochloric acid.

Third Analytical Reaction: The hydrogen test, or "*Marsh's*" *test.*—Generate hydrogen in the usual way from water by zinc and sulphuric acid, a bottle of about four or six ounces capacity being used, and a funnel-tube and short delivery-tube passing through the cork in the usual manner (see following figure). Dry the escaping hydrogen (except in rough experiments, when it is unnecessary) by adapting to the delivery-tube, by a pierced cork, a short piece of wider tubing filled with fragments of chloride of calcium, *a*. To the opposite end of the drying tube fit a piece of narrow tubing ten or twelve inches long, made of hard German glass, and having its aperture narrowed by drawing out in the flame of the blowpipe. When the hydrogen has been escaping for a sufficient number of minutes, and at such a rate as to warrant the operator in concluding that all the air originally existing in the bottle has been expelled, set light to the jet, and then pour eight or ten drops of the aqueous solution of arsenic, or three or four drops of the acid or alkaline solution of arsenic, previously prepared, into the funnel-tube, washing the liquid into the generating-bottle with a little water. The arsenic is at once reduced to the state of arsenicum, and the latter combines with some of the hydrogen to form hydride of arsenicum or arseniuretted hydrogen gas (AsH_3). Immediately hold a piece of earthenware or porcelain (the lid of a porcelain crucible, *b*, if at hand) in the hydrogen jet at the extremity of the delivery-tube; a brown spot of arsenicum is deposited on the porcelain. Collect several of these spots, and retain them for future comparison with antimonial spots (p. 181).

Fig. 35.



The Hydrogen Test for Arsenicum.

The separation of arsenicum in the flame is due to the decomposition of the arseniuretted hydrogen by the heat of combustion. The cool porcelain at once condenses the arsenicum, and thus prevents its oxidation to white arsenic, which would otherwise take place at the outer edge of the flame.

Hold a small beaker, *c*, or wide test-tube over the flame for a few minutes; a white film of arsenic (As_2O_3) will be slowly deposited, and may be further examined in contrast with a similar antimonial film (p. 181).

During these experiments the effect produced by the arsenical vapors on the color of the hydrogen-flame will have been noticed; they give it a dull livid tint. This is characteristic.

Apply the flame of a gas-lamp to the middle of the hard delivery-tube, *d*; the arseniuretted hydrogen, as before, is decomposed by the heat, but the liberated arsenicum (As_2) immediately condenses in the cool part of the tube beyond the flame, forming a dark metallic mirror. The tube may be removed and kept for comparison with the antimonial deposit.

Note I.—Zinc, like copper, frequently itself contains arsenicum. When a specimen free from arsenicum is met with, it should be reserved for analytical experiments, or a quantity of guaranteed purity should be purchased of the chemical-apparatus maker. Sulphuric acid is more easily obtained free from arsenic.

Note II.—In delicate and important applications of Marsh's test, magnesium may be substituted for zinc with safety, as arsenicum has not yet been, and is not likely to be, found in magnesium. Magnesium in rods is convenient for this purpose, and may be obtained from most dealers in chemicals.

Note III.—Sulphuric acid, which is often used for drying gases, decomposes arseniuretted hydrogen. Chloride of calcium is therefore the appropriate desiccating agent for this gas.

Fourth Analytical Reaction: Fleitmann's test.—Generate hydrogen by heating in a test-tube to near the boiling-point a strong solution of caustic soda or potash and some pieces of zinc (or aluminium).

($Zn + 2NaHO = H_2 + Na_2ZnO_2$—zincate of sodium.)

Add a drop of arsenical solution, and spread over the mouth of the tube a cap of filter-paper moistened with one drop of solution of nitrate of silver, Again heat the tube, taking care that the liquid itself shall not spirt up on to the cap. A plug of cotton-wool may even be placed in the mouth of the test-tube to prevent this spirting (Senier). The arsenic is reduced to arsenicum, the latter uniting with the hydrogen as in Marsh's test; and the arseniuretted hydrogen passing up through the cap reacts on the nitrate of silver, causing the production of a purplish-black spot.

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 3Ag_2.$$

Note I.—This reaction is particularly valuable, enabling the analyst to quickly distinguish arsenicum in the presence of its sister element antimony, which, although it combines with the hydrogen evolved from dilute acid and zinc, does not combine with the hydrogen evolved from solution of alkali and zinc, and therefore does not give the effect just described.

Note II.—Aluminium answers as well as zinc for Fleitmann's test

(Gatehouse), or magnesium may be used; or instead of zinc and alkali, weak sodium amalgam may be employed (Davy).

Fifth Analytical Reaction.—To a solution of chloride of tin in strong hydrochloric acid add a very small quantity of any arsenical solution. Arsenicum then separates, especially on the application of heat, giving the mixture a yellowish and then brownish hue or grayish-brown turbidity, or even a sediment of gray-brown flocks, according to the amount present. Much water prevents the reaction, its presence, therefore, must be avoided as far as possible; indeed a liquid saturated by hydrochloric acid gas gives best results. Arsenic in sulphuric or hydrochloric acid or in tartar emetic, etc., may be detected by this method. Nitrates, such as subnitrate of bismuth, must first be heated with sulphuric acid to remove the nitric radical before applying this reduction test for arsenicum. The stannous is converted to stannic salt during the reaction.

Distinction between Arsenious and Arsenic combinations.—The above tests are those of arsenicum, whether existing in the arsenious or arsenic condition, though from the latter the element is not generally eliminated so quickly as from the former. Of the following reactions, that with nitrate of silver at once distinguishes arsenious acid and other arsenites from arsenic acid and other arseniates.

Mem.—The exact nature of all these analytical reactions will be more fully evident if traced out by diagrams or equations.

Sixth Analytical Reaction.—Through an acidified solution of arsenic pass sulphuretted hydrogen; a yellow precipitate of sulphide of arsenicum or arsenious sulphide (As_2S_3) quickly falls. Add an alkaline hydrate or sulphydrate to a portion of the precipitate; it readily dissolves. The precipitate consequently would not be obtained on passing sulphuretted hydrogen through an alkaline solution of arsenic. To another portion of the precipitate, well drained, add *strong* hydrochloric acid; it is insoluble, unlike sulphide of antimony. Neither sulphide is soluble in the *weak* acid.

Note I.—Cadmium also affords a yellow sulphide in an acid solution by action of sulphuretted hydrogen, but this sulphide is insoluble in alkaline liquids. Under certain circumstances, tin, too, yields a yellow sulphide; but tin is otherwise easily distinguished (*vide* Tin).

Note II.—A trace of sulphide of arsenicum is sometimes met with in sulphur (distilled from arsenical pyrites). It may be detected by digesting the sulphur in solution of ammonia, filtering, and evaporating to dryness; a yellow residue of sulphide of arsenicum is obtained if that substance be present.

Seventh Analytical Reaction.—Through an acidified solution of arsenic acid, or any other arseniate, pass sulphuretted hydrogen; the arsenic compound is gradually reduced to the arsenions and a yellow precipitate of arsenious sulphide and sulphur ($As_2S_3 + S_2$) slowly falls, soluble in alkaline hydrates and sulphydrates.

Chemical Analogy of Sulphur and Oxygen.—The solubility of arsenious and arsenic sulphide in alkaline solutions is good evidence of the close chemical analogy between them and the corresponding oxygen compounds of arsenicum. The potassium arsenite and sulpharsenite, arseniate and sulph-arseniate, have the composition represented by the following formulæ:—

K_3AsO_3 K_3AsO_4
K_3AsS_3 K_3AsS_4;

and the corresponding ammonium and sodium salts have a similar composition:—

$$6AmHS + As_2S_3 = 2Am_3AsS_3 + 3H_2S$$
$$6AmHS + As_2S_5 = 2Am_3AsS_4 + 3H_2S.$$

Eighth Analytical Reaction.—To an aqueous solution of arsenic add two or three drops of solution of sulphate of copper, and then cautiously add diluted solution of ammonia, drop by drop, until a green precipitate is obtained. The production of this precipitate is characteristic of arsenicum. To a portion of the mixture add an acid; the precipitate dissolves. To another portion add alkali: the precipitate dissolves. These two experiments show the advantage of testing a suspected arsenical solution by litmus-paper before applying this reaction; if acid, cautiously adding alkali, if alkaline, adding acid, till neutrality is obtained. (Or a special copper reagent may be used; see a note to the Eleventh Analytical Reaction, below).

The precipitate is arsenite of copper ($Cu''HAsO_3$) or *Scheele's Green.* More or less pure, or mixed with acetate or, occasionally, carbonate of copper, it is very largely used as a pigment under many names, such as Brunswick Green and Schweinfurth Green, by painters, paper-stainers, and others.

Ninth Analytical Reaction.—Apply the test just described to a solution of arsenic acid or other arseniate; a somewhat similar precipitate of arseniate of copper is obtained.

Tenth Analytical Reaction.—Repeat the eighth reaction, substituting nitrate of silver for sulphate of copper; in this case *yellow* arsenite of silver (Ag_3AsO_3) falls, also soluble in acids and alkalies.

Eleventh Analytical Reaction.—Apply the test to a solution of arsenic acid or other arseniate; a *chocolate*-colored precipitate of arseniate of silver (Ag_3AsO_4) falls.

This reaction may be utilized for the detection of arsenic when occurring in ores and other substances as ordered by the U. S. Pharmacopœia in the case of *Antimonii Sulphidum Purificatum:*

"If 2 gm. of the salt be mixed and cautiously ignited, in a porcelain crucible, with 8 gm. of pure nitrate of sodium, and the fused mass boiled with 25 gm. of water, there will remain a residue which should be white, or nearly so, and not yellowish nor brownish (abs. of other metallic sulphides). On boiling the filtrate with an excess of nitric acid, until no more nitrous vapors are evolved, then dissolving in it 0.1 gm. of nitrate of silver, filtering again, if necessary, and cautiously pouring a few drops of water of ammonia on top, not more than a white cloud, but no red nor reddish precipitate, should appear at the line of contact of the two liquids (abs. of more than traces of arsenic)."

Copper and Silver Reagents for Arsenicum.—The last four reactions may be performed with increased delicacy and certainty of result if the copper and silver reagents be previously prepared in the following manner: To solution of pure sulphate of copper (about 1 part in 20 of water) add ammonia until the blue precipitate at first formed is nearly but not quite redissolved; filter and preserve the liquid as an arsenicum reagent, labelling it *solution of ammonio-sulphate of copper* (B. P.). Treat solution of nitrate of silver (about 1 part in 40) in the same way, and label it *solution of ammonio-nitrate of silver* (B. P.). The composition of these two salts will be referred to subsequently.

Arsenious and Arsenic Compounds.—While many reagents may be used for the detection of arsenicum, only nitrate of silver, as already stated, will readily indicate in which state of oxidation the arsenicum exists; for the two sulphides and the two copper precipitates, though differing in composition, resemble each other in appearance, whereas the two silver precipitates differ in color as well as in composition.

Soluble arseniates also give insoluble arseniates with solutions of salts of barium, calcium, zinc, and some other metals.

In group-testing, arsenicum, if existing as arsenic acid or other arseniate, is not readily affected by such tests as sulphuretted hydrogen or even hydrogen itself. Hence, if its presence in that state is suspected, the liquid under analysis should be warmed with a little sulphurous acid or oxalic acid, and then tested with sulphuretted hydrogen.

Antidote.—In cases of poisoning by arsenic or arsenical preparations, the most effective antidote is recently precipitated moist ferric hydrate (*Ferri Oxidum Hydratum*, U. S. P.). It is perhaps best administered in the form of a mixture or solution of ferric sulphate (*Liquor Ferri Tersulphatis*, U. S. P.) or perchloride of iron (*Liquor* or *Tinctura*) with carbonate of sodium—two or three ounces of the former to about one ounce of the crystals of the latter. Instead of the carbonate of sodium, about a quarter of an ounce of calcined magnesia may be used. (See *Ferri Oxidum Hydratum cum Magnesia*, U. S. P., page 148.) These quantities will render at least 10 grains of arsenic insoluble. Emetics should also be given, and the stomach-pump applied as quickly as possible.

The above statements regarding the antidote for arsenic may be verified by mixing the various substances together, filtering, and proving the absence of arsenicum in the filtrate by applying some of the foregoing tests.

Mode of Action of the Antidote.—The action of the carbonate of sodium or the magnesia is to precipitate ferric hydrate (Fe_26HO)—chloride of sodium ($NaCl$) or magnesium ($MgCl_2$) being formed, which are harmless, if not beneficial, under the circumstances. The reaction between the ferric hydrate and the arsenic results in the formation of insoluble ferrous arseniate.

$$\underset{\substack{\text{Ferric}\\\text{hydrate.}}}{2(Fe_26HO)} + \underset{\text{Arsenic.}}{As_2O_3} = \underset{\substack{\text{Ferrous}\\\text{arseniate.}}}{Fe_32AsO_4} + \underset{\text{Water.}}{5H_2O} + \underset{\substack{\text{Ferrous}\\\text{hydrate.}}}{Fe2HO}$$

The so-called Solution of Dialyzed Iron (see Index) is also, as might be expected from its composition, an antidote to arsenic. It should be administered with a little bicarbonate of either sodium or potassium, or with magnesia, or with any other salt which serves to neutralize any acid that may be present.

QUESTIONS AND EXERCISES.

249. What is the formula of a molecule of arsenicum?

250. In what form does arsenicum occur in nature?

251. Describe the characters of white arsenic.

252. Name the official preparations of arsenicum.

253. What proportion of arsenic (As_2O_3) is contained in *Liquor Potassii Arsenitis*, U. S. P., and in *Liquor Acidi Arseniosi*, U. S. P.?

254. By what method may arsenic be reduced to arsenicum?

255. Give the formulæ of arsenious and arsenic acids and anhydrides.

256. Explain, by diagrams, the reactions which occur in converting arsenic into Arseniate of Sodium by the process of the British Pharmacopœia.

257. Why is anhydrous instead of crystallized arseniate of sodium employed in the preparation of *Liquor Sodii Arseniatis*, U. S. P.?

258. In the preparation of Arseniate of Iron from ferrous sulphate and arseniate of sodium, why is acetate of sodium included?

259. Describe the manipulations necessary to obtain arsenic in its characteristic crystalline form.

260. How is Reinsch's test for arsenicum applied, and under what circumstances may its indications be fallacious?

261. Give the details of Marsh's test for arsenicum, and the precautions to be observed in its performance. Explain the reactions by diagrams?

262. What peculiar value has Fleitmann's test for arsenicum?

263. Describe the conditions under which sulphuretted hydrogen becomes a trustworthy test for arsenicum?

264. How may a trace of sulphide of arsenicum be detected in sulphur?

265. How are the salts of copper and silver applied as reagents for the detection of arsenicum?

266. How are arsenites distinguished from arseniates?

267. Mention the best antidote in cases of poisoning by arsenic, explain the process by which it may be most quickly prepared, and describe its action.

268. Do you know of any other antidote to arsenic? If so, describe the mode of administration.

ANTIMONY.

Symbol Sb (Stibium). Atomic weight 120.

Sources and Uses.—Antimony occurs in nature chiefly as sulphide, Sb_2S_3. The *crude* or *black antimony* of pharmacy is this native sulphide freed from impurities by fusion; it has a striated, crystalline, lustrous fracture; subsequently powdered it forms the grayish-black, crystalline *Antimonii Sulphidum*, U. S. P. When this powder is washed with solution of ammonia to remove any traces of sulphide of arsenicum and dried, it forms the *Antimonii Sulphidum Purificatum*, U. S. P. The metal is obtained from the sulphide by roasting, the resulting oxide being reduced with charcoal and carbonate of sodium. Metallic antimony is an important constituent of *Type-metal*, *Britannia metal* (tea and coffee pots, spoons, etc.), and the best varieties of *Pewter*. The old *pocula emetica*, or everlasting emetic cups, were made of antimony; wine kept in them for a day or two acquired a variable amount of emetic quality. The metal is not used in making the antimonial preparations of the Pharmacopœia, the sulphide alone being, directly or indirectly, employed for this purpose.

Antimony has very close chemical analogies with arsenicum. Its atom, in the common salts, exerts trivalent activity (*e. g.*, $SbCl_3$), but sometimes it is quinquivalent (*e. g.*, $SbCl_5$).

Antimony, like arsenicum, unites with iodine to form a tri-iodide (SbI_3). A bromide ($SbBr_3$) is also known.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Reactions having Synthetical Interest.*

Chloride of Antimony. Antimonious Chloride.

First Synthetical Reaction.—Boil half an ounce or less of sulphide of antimony with four or five times its weight of hydrochloric acid in a dish in a fume-chamber or in the open air; sulphuretted hydrogen is evolved, and solution of chloride of antimony, $SbCl_3$, is obtained.

$$\underset{\text{Sulphide of antimony.}}{Sb_2S_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Chloride of antimony.}}{2SbCl_3} + \underset{\text{Sulphuretted hydrogen.}}{3H_2S}$$

This solution, cleared by subsidence, is what is commonly known as *Butter of antimony* (*Liquor Antimonii Chloridi*, B. P.). If pure sulphide has been used in its preparation, the liquid is nearly colorless; but much of that met with in veterinary pharmacy is simply a by-product in the generation of sulphuretted hydrogen from native sulphide of antimony and hydrochloric acid, and is more or less brown from the presence of chloride of iron. It not unfrequently darkens in color on keeping; this is due to absorption of oxygen from the air and conversion of light-colored ferrous into dark-brown ferric chloride or oxychloride.

True butter of antimony ($SbCl_3$) is obtained on evaporating the above solution to a low bulk, and distilling the residue. The butter condenses (as a white crystalline semi-transparent mass in the neck of the retort); at the close of the operation it may be easily melted and run down in a bottle, which should be subsequently well stoppered.

Pentachloride of antimony ($SbCl_5$), or *antimonic chloride*, is a fuming liquid, obtained on passing chlorine over the lower chloride.

Oxychloride of Antimony. Antimonious Oxychloride.

Second Synthetical Reaction.—Pour the solution of chloride of antimony produced in the last reaction into several ounces of water; a white precipitate of oxychloride of antimony ($2SbCl_3,5Sb_2O_3$) falls, some chloride of antimony remaining in the supernatant acid liquid.

This is the old *pulvis Algarothi*, *pulvis angelicus*, or *mercurius vitæ*. On standing under water it gradually becomes crystalline.

$$\underset{\text{Chloride of antimony.}}{12SbCl_3} + \underset{\text{Water.}}{15H_2O} = \underset{\text{Oxychloride of antimony.}}{2SbCl_3,5Sb_2O_3} + \underset{\text{Hydrochloric acid.}}{30HCl}$$

Oxide of Antimony. Antimonious Oxide.

Well wash the precipitate with water, by decantation (*vide* p. 108), and add solution of carbonate of sodium; the chloride remaining with the oxide is thus decomposed, and oxide of antimony (Sb_2O_3) alone remains. This is *Antimonii Oxidum*, U. S. P. It is of a light buff or grayish-white color, or quite white if absolutely free from iron, insoluble in water, soluble in hydrochloric acid, fusible at a low red heat. The moist oxide of antimony may be well washed and employed for the next reaction, or dried over a water-bath. At temperatures above 212° oxygen is absorbed, and other oxides of antimony formed. The presence of the latter is detected on boiling the powder in solution of acid tartrate of potassium, in which oxide of antimony (Sb_2O_3) is soluble, but *antimonic anhydride* (Sb_2O_5) and the double oxide or so-called *antimonious anhydride* (Sb_4O_8) are insoluble.

$$\underset{\text{Oxychloride of antimony.}}{2SbCl_3,5Sb_2O_3} + \underset{\text{Carbonate of sodium.}}{3Na_2CO_3} = \underset{\text{Oxide of antimony.}}{6Sb_2O_3} + \underset{\text{Chloride of sodium.}}{6NaCl} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

The higher oxide of antimony (Sb_2O_5), termed antimonic oxide or anhydride, corresponding with arsenic anhydride, is obtained on decomposing the pentachloride by water, or on boiling metallic antimony with nitric acid. The variety obtained from the chloride differs in saturating power from that obtained from the metal, and is termed metantimonic (*μετα*, *meta*, beyond).

Tartar Emetic.

Third Synthetical Reaction.—Mix the moist oxide of antimony obtained in the previous reaction with about an equal quantity of cream of tartar (6 of the latter to 5 of the dry oxide) and sufficient water to form a paste; set aside for a day to facilitate complete combination; boil the product with water, and filter; the resulting liquid contains the double tartrate of antimony and potassium ($KSbC_4H_4O_7$), potassio-tartrate of antimony, tartrated antimony, or tartar emetic (emetic, from *ἐμέω*, *emeō*, I vomit; tartar, from *τάρταρος*, *tartaros*, see Index).

$$\underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Oxide of antimony.}}{Sb_2O_3} = \underset{\text{Tartar emetic.}}{2KSbC_4H_4O_7} + \underset{\text{Water.}}{H_2O}$$

On evaporation the salt is obtained in colorless transparent triangular-faced crystals of the above composition, with a molecule of water of crystallization, forming the *Antimonii et Potassii Tartras*, U. S. P., $2KSbOC_4H_4O_6,H_2O$.

The formula for tartar emetic is apparently inconsistent with the general formula for tartrates ($R'R'C_4H_4O_6$); this will be subsequently fully explained in connection with Tartaric Acid. The salt appears to be an oxytartrate ($KSbC_4H_4O_6O$).

Tartar emetic is soluble in water, and slightly so in proof-spirit. Dissolved in sherry wine it forms the official *Vinum Antimonii*, U. S. P.

Sulphurated Antimony. Oxysulphide of Antimony.

Fourth Synthetical Reaction.—Boil a few grains of sulphide of antimony with solution of soda in a test-tube, and filter (or larger quantities in larger vessels, 1 part of sulphide to 12 of soda, and 30 of water for 2 hours, frequently stirring, and occasionally replacing water lost by evaporation). Into the filtrate, before cool, stir diluted sulphuric acid until the liquid is slightly acid to test-paper; a brownish-red precipitate of oxysulphide of antimony, *Antimonium Sulphuratum*, U. S. P., falls; filter, wash, and dry over a water-bath. It is a mixture of sulphide of antimony (Sb_2S_3) with a small and variable amount of oxide (Sb_2O_3). The oxide results from the double decomposition of sulphide of antimony and soda.

If a small quantity of sulphur be boiled with the sulphide of antimony in solution of soda, the precipitate on addition of sulphuric acid will have a much brighter color, chiefly on account of the presence of a higher sulphide having a yellow color (Sb_2S_5).

These are some of the many varieties of *mineral kermes*, so called from their similarity in color to the *insect kermes*. Kermes is the name, now obsolete, of the *Coccus Ilicis*, a sort of cochineal insect, full of reddish juice, and used for dyeing from the earliest times. The color of the precipitate is affected by the temperature as well as state of dilution of the alkaline liquid when the acid is added. When the alkaline liquid is boiled, especially if long exposed to air, oxygen is absorbed by some of the antimony, whose sulphur uniting with the trisulphate forms a portion of the lighter yellow pentasulphide. *Kermes mineral* thus varies much in proportion of oxide and of pentasulphide as well as in the physical condition of its trisulphide.

Explanation of Process.—The sulphides and oxides of antimony, like those of arsenicum, react with the sulphides and oxides of certain metals to form soluble salts (Na_3SbS_3 and Na_3SbO_3). The former is deposited in yellow tetrahedral crystals when such an alkaline solution is set aside to slowly cool.

$$\underset{\substack{\text{Sulphide of}\\\text{antimony.}}}{2Sb_2S_3} + \underset{\text{Soda.}}{6NaHO} = \underset{\substack{\text{Sulph-antimonite}\\\text{of sodium.}}}{2Na_3SbS_3} + \underset{\substack{\text{Oxide of}\\\text{antimony.}}}{Sb_2O_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\substack{\text{Oxide of}\\\text{antimony.}}}{Sb_2O_3} + \underset{\text{Soda.}}{6NaHO} = \underset{\substack{\text{Antimonite}\\\text{of sodium.}}}{2Na_3SbO_3} + \underset{\text{Water.}}{3H_2O}$$

In the hot solutions of these salts sulphide and oxide of antimony are soluble, and are reprecipitated in an indefinite state of combination, partially on cooling, or wholly on the addition of acid. The acid also decomposes the oxysalt with precipitation of oxide, and the sulphur salt with precipitation of orange sulphide of antimony. The acid is added to the liquid before much oxysulphide has deposited (that is, before the solution is cool), in order to insure uniformity of product.

$2Na_3SbS_3$	+	$3H_2SO_4$	=	$3Na_2SO_4$	+	Sb_2S_3	+	$3H_2S$
Sulph-antimonite of sodium.		Sulphuric acid.		Sulphate of sodium.		Sulphide of antimony.		Sulphuretted hydrogen.
$2Na_3SbO_3$	+	$3H_2SO_4$	=	$3Na_2SO_4$	+	Sb_2O_3	+	$3H_2O$
Antimonite of sodium.		Sulphuric acid.		Sulphate of sodium.		Oxide of antimony.		Water.

The oxide and sulphide indicated in these equations, together with excess of sulphide of antimony originally dissolved by the alkaline liquid, are all precipitated when the acid is added, and form the *Sulphurated Antimony* of the Pharmacopœia, a reddish-brown powder, readily dissolved by caustic soda, also by hydrochloric acid, with the evolution of sulphuretted hydrogen and the separation of a little sulphur. Its antimony is detected by dissolving the powder in hydrochloric acid or in solution of acid tartrate of potassium, and passing sulphuretted hydrogen through the liquid, as described in the first analytical reaction.

The previous four synthetical reactions illustrate the official processes for the respective substances. The solution of chloride of antimony is only used in the preparation of oxide; the oxide, besides its use in the preparation of tartar emetic, is mixed with twice its weight of phosphate of calcium (purified bone-earth) to form *Pulvis Antimonialis*, U. S. P., or "*James's Powder.*"

The *sulphides* and *hydride* of antimony are incidentally mentioned in the following analytical paragraphs.

(*b*) *Reaction having Analytical Interest* (*Tests*).

First Analytical Reaction.—Through an acidified antimonial solution pass sulphuretted hydrogen; an orange precipitate of amorphous sulphide of antimony falls. It has the same composition as the crystalline black sulphide (Sb_2S_3), into which, indeed, when dried, it is quickly converted by heat. Like sulphide of arsenicum, it is soluble in alkaline solutions. Collect a portion on a filter, and, when well drained, add *strong* hydrochloric acid; it dissolves—unlike sulphide of arsenicum.

A higher sulphide of antimony (Sb_2S_5), corresponding to the higher sulphide of arsenicum, exists. It is formed on passing sulphuretted hydrogen through an acidified solution of the higher chloride ($SbCl_5$), or on boiling black sulphide of antimony and sulphur with an alkali, and decomposing the resulting filtered liquid by an acid.

Note.—The arsenious and antimonious compounds are those chiefly employed in medicine; arseniates of sodium and iron are, however, sometimes employed. The arseniates and rarely an antimoniate are useful in analysis, and the antimonic chloride in chemical research. The higher compounds of both elements are noticed here chiefly to draw attention to the close analogy existing between arsenicum and antimony, an analogy carried out in the numerous other compounds of these elements.

Second Analytical Reaction.—Dilute two or three drops of the solution of chloride of antimony with water; a precipitate of oxychloride occurs, the formation of which has been explained under the similar synthetical reaction. The occurrence of this precipitate distinguishes antimony from arsenicum, but is a reaction that cannot be fully relied upon in analysis, because requiring the presence of too much material and the observance of too many conditions. Add a sufficient quantity of hydrochloric acid to dissolve the precipitate, and boil a piece of copper in the solution, as directed in the corresponding test for arsenicum (*vide* page 169); antimony is deposited on the copper. Wash, dry, and heat the copper in a test-tube as before; the antimony, like the arsenicum, is volatilized off the copper and condenses on the side of the tube as white oxide, but the sublimate, from its low degree of volatility, condenses close to the copper; moreover, it is destitute of crystalline character—that is to say, it is *amorphous* (*α*, *a*, without; *μορφή*, *morphē*, shape).

Shake out the copper, and boil water in the tube for several minutes. Do the same with the arsenical sublimate similarly obtained. The deposit of arsenic slowly dissolves, and may be recognized in the solution by ammonio-nitrate of silver; the antimonial sublimate is insoluble.

Third Analytical Reaction.—Perform the experiments described under Marsh's test for arsenicum (pp. 169, 170), carefully observing all the details there mentioned, but using a few drops of solution of chloride of antimony or tartar emetic instead of the arsenical solution. Antimoniuretted hydrogen, or hydride of antimony (SbH_3), is formed and decomposed in the same way as arseniuretted hydrogen.

To one of the arsenicum spots on the porcelain lid (p. 170) add a drop of a solution of "chloride of lime" (bleaching-powder); it quickly dissolves. Do the same with an antimony spot; it is unaffected.

Heat more quickly causes the volatilization of an arsenicum than an antimony spot; sulphydrate of ammonium more readily dissolves the antimony than the arsenicum.

Boil water for several minutes in the beaker or wide test-tube containing the arsenious sublimate (page 170); it slowly dissolves, and may be recognized in the solution by the yellow precipitate given on the addition of solution of ammonio-nitrate of silver. The antimonial sublimate, similarly treated, does not dissolve.

Pass a slow current of sulphuretted hydrogen through the delivery-tube removed from the hydrogen-apparatus (page 170), and, when the air may be considered to have been expelled from the tube, gently heat that portion containing the deposit of arsenicum; the latter will be converted into a *yellow* sublimate of sulphide of arsenicum. Remove the tube from the sulphuretted-hydrogen apparatus, and repeat the experiment with a similar antimony deposit; it is converted into *orange* sulphide of antimony, which, moreover, owing to inferior volatility, condenses nearer to the flame than sulphide of arsenicum.

Pass dry hydrochloric acid gas through the two delivery-tubes. This is accomplished by adapting first one tube and then the other by a cork to the test-tube containing a few lumps of common salt, on which a little sulphuric acid is poured during the momentary removal of the cork. The sulphide of antimony dissolves and disappears; the sulphide of arsenicum is unaffected.

Thorough conception of the chemistry of arsenicum and antimony will be obtained on constructing equations or diagrams descriptive of each of the foregoing reactions.

Antidote.—The introduction of poisonous doses of antimonials into the stomach is fortunately quickly followed by vomiting. If vomiting has not occurred, or apparently to an insufficient extent, any form of tannic acid may be administered (infusion of tea, nutgalls, cinchona, oak-bark, or other astringent solutions or tinctures), an insoluble tannate of antimony being formed, and absorption of the poison consequently somewhat retarded. The stomach-pump must be applied as quickly as possible.

Recently precipitated moist ferric hydrate is also, according to T. and H. Smith, a perfect absorbent of antimony from its solutions, the chemical actions being probably, they say, similar to that which takes place between ferric hydrate and arsenious anhydride. It may be given in the form of a mixture of perchloride of iron with either carbonate of sodium or magnesia.

These statements may be verified by mixing together the various substances, filtering, and testing the filtrate for antimony in the usual manner.

DIRECTIONS FOR APPLYING THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE OF THE ELEMENTS ARSENICUM AND ANTIMONY.

Acidify the liquid with hydrochloric acid, and pass through it sulphuretted hydrogen—

A *yellow* precipitate indicates arsenicum.

An *orange* precipitate indicates antimony.

The result may be confirmed by the application of other tests.

DIRECTIONS FOR APPLYING THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF BOTH ARSENICUM AND ANTIMONY.

Acidify a small portion of the liquid with hydrochloric acid, and pass through it sulphuretted hydrogen.

Note I.—If the precipitate by sulphuretted hydrogen is unmistakably orange, antimony may be put down as present, and arsenicum only further sought by the application of Fleitmann's test to the solution of the sulphide in aqua regia* freed from sulphur by boiling, or, better, to the original solution.

Note II.—Sulphide of antimony is far less readily soluble than sulphide of arsenicum in solution of carbonate of ammonium. But this fact possesses limited analytical value; for the color of the sulphides is already sufficient to distinguish the one from the other when they are unmixed; and when mixed, much sulphide of antimony will prevent a little sulphide of arsenicum from being dissolved by the alkaline carbonate, while much sulphide of arsenicum will carry a little sulphide of antimony into the solution. When the proportions are, apparently, from the color of the precipitate, less wide, solution of carbonate of ammonium will be found useful in roughly separating the one sulphide from the other. On filtering and neutralizing the alkaline solution by an acid, the yellow sulphide of arsenicum is reprecipitated. The orange sulphide of antimony will remain on the filter.

Note III.—Solution of bisulphite of potassium is said by Wöhler to be a good reagent for separating the sulphides of arsenicum and antimony, the former being soluble, the latter insoluble in the liquid.

Note IV.—Another reagent for separating the sulphides of arsenicum and antimony is *strong* hydrochloric acid. As little water as possible must be present. On boiling, the sulphide of antimony dissolves, while the sulphide of arsenicum remains insoluble. The liquid slightly diluted, filtered, more water added, and sulphuretted hydrogen again transmitted, gives orange sulphide of antimony. The process should previously be tried on the precipitated mixed sulphides. The presence of arsenicum may be confirmed by the application of Fleitmann's test to the original solution.

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* *Aqua regia* is a mixture of fifteen parts hydrochloric and four parts nitric acid. It was so called from its property of dissolving gold, the "king" of metals.

Note V.—If the precipitate by sulphuretted hydrogen is unmistakably yellow, arsenicum may be put down as present, and any antimony detected by the previous or one of the following two processes. These two processes are rather long, and require much care in their performance, but are useful, because a small quantity of antimony in much arsenicum, or *vice versâ*, may be detected by their means.

First Process.—Generate hydrogen and pass it through a small wash-bottle containing solution of acetate of lead, to free the gas from any trace of sulphuretted hydrogen it may possess, and then through a dilute solution of nitrate of silver contained in a test-tube. When the apparatus is in good working order, pour into the generating-bottle the solution to be examined, adding it gradually to prevent violent action. After the gas has been passing for five or ten minutes, examine the contents of the nitrate-of-silver tube; arsenicum, if present, will be found in the solution in the state of arsenious acid,

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 3Ag_2;$$

while antimony, if present, will be found in the black precipitate that has fallen, according to the following equation:—

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

The arsenious radical may be detected in the clear, filtered, supernatant liquid, which still contains much nitrate of silver, by cautiously neutralizing with a very dilute solution of ammonia, or by adding a few drops of solution of ammonio-nitrate of silver, yellow arsenite of silver being produced. The antimony may be detected by washing the black precipitate, boiling it in an open dish with solution of tartaric acid, acidulating with hydrochloric acid, filtering, and passing sulphuretted hydrogen through the solution—the orange sulphide of antimony being precipitated (Hofmann).

Second Process.—Obtain the metallic deposit in the middle of the delivery-tube, as already described under Marsh's test. Act on the deposit by sulphuretted hydrogen gas, and then by hydrochloric acid gas, as detailed in the third analytical reaction of antimony (p. 181). If both arsenicum and antimony are present, the deposit, after the action of sulphuretted hydrogen, will be found to be of two colors, the yellow sulphide of arsenicum being usually further removed from the heated portion of the tube than the orange sulphide of antimony. Moreover, subsequent action of hydrochloric acid gas causes disappearance of the antimonial deposit, which is converted into chloride of antimony and carried off in the stream of gas.

The chief objection to this process is the liability of the operator mistaking sulphur, deposited from the sulphuretted hydrogen gas by heat, for sulphide of arsenicum. But the presence or absence of arsenicum is easily confirmed by applying Fleitmann's test to the original solution, while the process is most useful for the detection of a small quantity of a salt of antimony when mixed with much of an arsenical compound.

The laboratory student may now proceed to the analysis of aqueous solution of salts of any of the metallic elements hitherto considered. The method followed may be that for the separation of the previous three groups, sulphuretted hydrogen being first passed through the solution to throw out arsenicum and antimony. The whole scheme of analysis is given on the next page. Three or four solutions should be examined before proceeding to the last group of metals.

Learners who have no opportunity of working at practical analysis will gain much knowledge by endeavoring not to remember, but to understand these methods of separating elements from each other in a solution containing several compounds.

QUESTIONS AND EXERCISES.

269. What is the composition and source of the *Black Antimony* of pharmacy?

270. In what alloys is metallic antimony a characteristic ingredient?

271. What is the quantivalence of antimony as far as indicated by the formulæ of the official preparations?

272. By a diagram show how "Butter of antimony" is prepared.

273. Write out equations or diagrams expressive of the reactions which occur in converting chloride of antimony into oxide.

274. What is the formula of Tartar Emetic?

275. Explain the official process for the preparation of Oxysulphide of Antimony (*Antimonium Sulphuratum*, U. S. P.) by aid of diagrams.

276. Give a comparative statement of the tests for arsenicum and antimony.

277. How is antimony detected in the presence of arsenicum?

278. How may arsenicum and iron be distinguished analytically?

279. Describe a method by which antimony, magnesium, and iron may be separated from each other.

280. Draw out an analytical chart for the examination of an aqueous liquid containing salts of arsenicum, zinc, calcium, and ammonium.

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Acidify with HCl, and pass H_2S through the solution; filter.

<table>
<tr>
<td rowspan="4">Precipitate
As Sb.
Wash, separate by carbonate of ammonium, or by strong HCl; or dissolve in a few drops of hydrochloric and nitric acids, and examine by Hofmann's method (p. 184).</td>
<td colspan="7">Filtrate
Fe Al Zn Ba Ca Mg K Na Am.
Add AmHO;* AmHS; stir, filter.</td>
</tr>
<tr>
<td colspan="3">Precipitate†
Fe Al Zn.
Wash, dissolve in HCl, boil with HNO_3 (p. 157), add KHO in excess,‡ stir, filter.</td>
<td colspan="4">Filtrate
Ba Ca Mg K Na Am.
Add Am_2CO_3, boil, filter.</td>
</tr>
<tr>
<td rowspan="2">Precipitate
Fe.
Examine orig. solution for ferrous or ferric state.</td>
<td colspan="2">Filtrate
Al Zn.
Neut. by HCl, add AmHO, stir, filter.</td>
<td colspan="2">Precipitate
Ba Ca.
Dissolve in $HC_2H_3O_2$, add K_2CrO_4, filter.</td>
<td colspan="2">Filtrate
Mg K Na Am.
Add Am_2HPO_4, shake, filter.</td>
</tr>
<tr>
<td>Ppt.
Al.</td>
<td>Sol.
Zn.</td>
<td>Precipitate
Ba.</td>
<td>Filtrate
Ca.</td>
<td>Precipitate
Mg.</td>
<td>Filtrate
Am Na K.
(page 199).</td>
</tr>
</table>

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* It is not usually necessary here to add NH_4Cl to keep Mg in solution, the HCl with some of the NH_4HO commonly giving sufficient NH_4Cl for this purpose.

† Much time may sometimes be saved by carefully remembering the color of the various hydrates and sulphides precipitated. Thus, if the AmHS precipitate is white, iron cannot be present, and AmHO, for Al and Zn, may be at once added to the hydrochloric solution of the precipitate. The group-tests in this Table are H_2S, AmHS, and Am_2CO_3.

‡ The pupil should vary the process sometimes, as described in the foot-notes on pages 159 and 161. The treatment of other groups should occasionally be varied. By remembering the reactions on which analytical processes are based a pupil may often devise modified processes, and thus frequently save time, avoid working in one groove only, and acquire broader chemical views.

COPPER, MERCURY, LEAD, SILVER.

These metals, like arsenicum and antimony, are precipitated from acidified solutions by sulphuretted hydrogen, in the form of sulphides; but the sulphides, unlike those of arsenicum and antimony, are insoluble in alkalies. The atom of copper is usually bivalent, Cu''; mercury bivalent in the mercuric salts, Hg'', and univalent in the mercurous salts, Hg'; lead sometimes quadrivalent, Pb'''', but generally exerting only bivalent activity, Pb''; and silver univalent, Ag'.

COPPER.

Symbol Cu. Atomic weight 63.2.

Source.—The commonest ore of this metal is *copper pyrites*, a double sulphide of copper and iron, raised in Cornwall; Australia and Russia supply *malachite*, a mixed carbonate and hydrate; much ore is also imported from South America. It is smelted in enormous quantities at Swansea, South Wales, a locality peculiarly fitted for the operation on account of its proximity to the coal-fields and its position as a sea-coast town—these advantages at all times insuring cheap fuel and freightage to the different metallurgical establishments. An economical method of smelting copper pyrites and other sulphides has recently been introduced by Hollway. After the sulphide is once melted air is driven, not over, as usual, but through the mass; the combustion of the sulphur then becomes self-supporting and is greatly accelerated.

Alchemy.—The alchemists termed this metal *Venus*, perhaps on account of the beauty of its lustre, and gave it her symbol ♀, a compound hieroglyphic also indicating a mixture of gold ⊙ and a certain hypothetical substance called acrimony ✠, the corrosive nature of which was symbolized by the points of a Maltese cross. To this day the blue show-bottle in the shop-window of the pharmacist is occasionally ornamented by such a symbol, indicative, possibly, of the fact that the blue liquid in the vessel is a preparation of copper.

Coinage.—The material of British copper coinage is now a bronze mixture composed, in 100 parts by weight, of 95 copper, 4 tin, and 1 zinc, the same as in the copper coinage of France. The penny is coined at the rate of 48 pence in one pound avoirdupois, of 7000 grains, or 453.6 grammes; the halfpenny at 80 in the pound avoirdupois, and the farthing at 160. British bronze coins are a legal tender in payments to the amount of 1*s.*

Metallic Copper, U. S. P., occurs "in slender wire, or thin foil cut into strips."

Quantivalence.—Copper forms two classes of salts; in one the atom is bivalent (Cu''), in the other it exerts univalent activity (Cu_2'). The former are of primary importance, the latter being for the most part unstable and wanting in technical interest. Their compounds are distinguished as cupric and cuprous; but those of the higher class only have general interest, and will be almost exclusively alluded to in the following paragraphs. Cuprous iodide (Cu_2I_2) will subsequently be referred to as a convenient form in which to remove iodine from solution, while the formation of cuprous oxide (Cu_2O), under given circumstances, will come under notice as an indicator of the presence of sugar in a liquid.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

The processes for the following salts include the only synthetical reactions having any medical or pharmaceutical interest: 1, cupric oxide, the black oxide of copper, prepared by heating fragments of copper to low redness on a piece of earthenware in an open fire; 2, cupric sulphate, the common sulphate of copper, prepared by boiling black oxide and about an equal weight of sulphuric acid in water, filtering, and setting aside the solution so that crystals may form on cooling; and 3, ammonio-sulphate of copper, for the preparation of which see p. 174; also p. 189.

$$\underset{\text{Copper.}}{Cu_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Cupric oxide.}}{2CuO}$$

$$\underset{\text{Cupric oxide.}}{CuO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Cupric sulphate.}}{CuSO_4} + \underset{\text{Water.}}{H_2O}$$

Sulphate of Copper (*Cupri Sulphas*, U. S. P.) ($CuSO_4,5H_2O$), *blue vitriol*, *bluestone*, or *cupric sulphate*, is the only copper salt of much importance in Pharmacy. It is a by-product in silver-refining ($2Ag_2SO_4 + Cu_2 = 2CuSO_4 + 2Ag_2$). A little is also formed in roasting copper pyrites. In the latter case some sulphide of iron and the sulphide of copper are oxidized to sulphates; but the low red heat finally employed decomposes the sulphate of iron, while the sulphate of copper is unaffected; it is purified by crystallization from a hot aqueous solution, though frequently much sulphate of iron remains in the crystals. Sulphate of copper results on dissolving in diluted sulphuric acid the black oxide (CuO) obtained in annealing copper plates (see the foregoing equations); it may also be prepared by boiling copper with three times its weight of sulphuric acid ($2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$), diluting, filtering, evaporating, and crystallizing. In this process a little black sulphide of copper is formed.

Anhydrous Sulphate of Copper ($CuSO_4$) is a yellowish-white powder prepared by depriving the ordinary blue crystals of sulphate of copper of their water of crystallization by exposing them to a temperature of about 400° F. It is used in testing alcohol and similar spirituous liquids for water, becoming blue if the latter be present.

Verdigris (from *verde-gris*, Sp. green-gray) is a Subacetate or Oxyacetate of Copper (B. P.) ($Cu_2O2C_2H_3O_2$), obtained by exposing alternate layers of copper and fermenting refuse grape-husks to the action of air. Digested with twice its weight of acetic acid and a little water, the mixture being evaporated to dryness and the residue dissolved in water, it forms a Solution of Acetate of Copper ($Cu2C_2H_3O_2,H_2O$), from which deep-green prismatic crystals of the acetate (*Cupri Acetas*, U. S. P.) may be obtained.

The modes of forming *cupric sulphide*, *hydrate*, *oxide*, *ferrocyanide*, and *arsenite*, as well as the precipitation of *metallic copper*, are incidentally alluded to in the following analytical paragraphs.

(*b*) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a copper salt (sulphate, for example); black cupric sulphide (CuS) falls.

Second Analytical Reaction.—Add sulphydrate of ammonium to an aqueous copper solution; cupric sulphide is again precipitated, insoluble in excess.

Note.—Cupric sulphide is not altogether insoluble in sulphydrate of ammonium if free ammonia or much ammoniacal salt be present; it is quite insoluble in the fixed alkaline sulphides.

Third Analytical Reaction.—Immerse a piece of iron or steel, such as the point of a penknife or a piece of wire, in a few drops of a copper solution; the copper is deposited, of characteristic color, an equivalent quantity of iron passing into solution.

By this reaction copper may be recovered on the larger scale from waste solutions, old hoop or other scrap iron being thrown into the liquors.

Fourth Analytical Reaction.—Add ammonia to a cupric solution; cupric hydrate ($Cu2HO$) of a light-blue color is precipitated. Add excess of ammonia; the precipitate is redissolved, forming a blue solution of ammonio-salt of copper, so deep in color as to render ammonia an exceedingly delicate test for this metal.

An ammonio-sulphate of copper may be obtained in large crystals by adding strongest solution of ammonia to powdered sulphate of copper until the salt is dissolved, placing the liquid in a test-glass or cylinder, cautiously pouring in twice its volume of strong alcohol or methylated spirit, taking care that the liquids do not become mixed, tying over the vessel with bladder, and setting aside for some weeks in a cool place (Wittstein.) The constitution of ammonio-sulphate and other ammonio-salts of copper and corresponding salts of silver will be alluded to in connection with "white precipitate," the official "ammoniated mercury."

Cuprum Ammoniatum is an ammonio-sulphate of copper prepared by rubbing together sulphate of copper and carbonate of ammonium until effervescence ceases, and drying the product.

Fifth Analytical Reaction.—Add solution of potash or soda to a cupric solution; cupric hydrate ($Cu2HO$) is precipitated, insoluble in excess. Boil the mixture in the test-tube; the hydrate is decomposed, losing the elements of water, and becoming the black anhydrous oxide (CuO).

Sixth Analytical Reaction.—Add solution of ferrocyanide of potassium (K_4Fcy) to an aqueous cupric solution; a reddish-brown precipitate of cupric ferrocyanide (Cu_2Fcy) falls. This is an extremely delicate test for copper.

Seventh Analytical Reaction.—To a cupric solution add solution of arsenic, and cautiously neutralize with alkali; green cupric arsenite ($CuHAsO_3$) falls.

Note.—This precipitate has been already mentioned under arsenicum. An arsenicum salt is thus a test for copper as a copper salt is for arsenicum—a remark that may obviously be extended to most analytical reactions; for the *body acted upon characteristically by a reagent is as good a test for the reagent as the reagent is for it;* indeed it becomes a reagent when the other body is the object of search. Most copper salts color flame green, the chloride blue.

Antidotes.—In cases of poisoning by compounds of copper, iron filings should be administered, the action of which has just been explained (see third analytical reaction). Ferrocyanide of potassium may also be given (see sixth analytical reaction). Albumen forms with copper a compound insoluble in water; hence raw eggs should be swallowed, vomiting being induced, or the stomach-pump applied as speedily as possible.

QUESTIONS AND EXERCISES.

281. What are the analytical relations of copper, mercury, lead, and silver to each other and to arsenicum and antimony?

282. Name the sources of copper.

283. What proportion of copper is contained in English and French "copper" coins?

284. Give diagrams showing how Sulphate of Copper is prepared on the small and large scales.

285. Work out a sum showing how much Crystallized Sulphate of Copper may be made from 100 parts of sulphide.—*Ans.* 261¼ parts.

286. How may Oxide of Copper be prepared?

287. Mention the formula of Verdigris.

288. Name a good clinical test for copper.

289. What is the analytical position of copper?

290. Mention the chief tests for copper.

291. How may copper be separated from arsenicum?

292. Why is finely divided iron an effective antidote in cases of poisoning by copper?

MERCURY.

Symbol Hg. Atomic weight 199.7.

Molecular weight 199.7 (*not* double the atomic weight).

Source.—Mercury occurs in nature as sulphide (HgS), forming the ore *cinnabar* (an Indian name expressive of something red), and is obtained from Spain, California, Eastern Hungary, China, Japan, and Peru.

Preparation.—The metal is separated by roasting off the sulphur and then distilling, or, better, distilling with lime, which combines with and retains the sulphur.

Properties.—Mercury (*Hydrargyrum*, U. S. P.) is a silver-white lustrous metal, liquid at common temperatures. It boils at 662° F., and at —40° F. solidifies to a malleable mass of octahedral crystals. When quite free from other metals it does not tarnish, its globules roll freely over a sheet of white paper without leaving any streak or losing their spherical form, and when boiled with strong solution of sodium hyposulphite it does not lose its lustre and does not acquire more than a slightly yellowish shade.

Formula.—The formula of the mercury molecule is Hg and not Hg_2, because (at all events at the high temperature at which alone the weight of its vapor can be determined) two volumes, which if hydrogen would weigh two parts (H_2) or oxygen thirty-two parts (O_2), in the case of mercury vapor weigh only two hundred parts (Hg); that is, only once the atomic weight, not twice. That 200, and not 100, is the atomic weight of mercury is shown by the fact that 200 is the minimum proportion relative to 1 of hydrogen in which mercury combines, and by its relations to heat. Still it is difficult to imagine an atom existing in the free state in nature; and the suggestion has been made that (as is proved to be the case with sulphur) mercury, as we know it, is in abnormal condition, and that if the weight of its vapor could be taken at a lower temperature, or under some other condition, its molecular weight might be found to be 400. Similar remarks may be made respecting zinc, the molecular weight of which, so far as we know, is identical with its atomic weight.

Medicinal Compounds.—The compounds of mercury used in medicine are all obtained from the metal. The metal itself, rubbed with chalk and sugar of milk, or with confection of roses and powdered liquorice-root, or with lard and suet, until globules are not visible *to the unaided eye*, is often used in medicine. The preparations are: the *Hydrargyrum cum Creta*, U. S. P., or "Gray Powder;" *Massa Hydrargyri*, U. S. P., "Blue Mass" or "Blue Pill;" and *Unguentum Hydrargyri*, U. S. P., or "Blue Ointment." There are also a Compound Ointment, a Plaster of Mercury, a Plaster of Ammoniacum and Mercury, a Liniment, and a Suppository. Their therapeutic effects are probably due not to the large quantity of metallic mercury in them, but to the small quantities of black and red oxide which occur in them through the action of the oxygen of the air on the finely-divided metal. The proportion of oxide or oxides varies according to the age of the specimen.

All these medicinal preparations of metallic mercury are indefinite and unsatisfactory, and that through no fault of the pharmacist. They much need investigation by therapeutists. Here, as in many similar cases, if Medicine would first ascertain her own requirements and then make them known, her handmaid Pharmacy would be found quite capable of supplying them.

Mercurous and Mercuric Compounds.—Mercury combines with other elements and radicals in two proportions; those compounds in which the other, acidulous, radicals are in the lesser amount are termed *mercurous*, the higher being *mercuric*. Thus, calomel (HgCl*) is mercurous chloride, while corrosive sublimate ($HgCl_2$) is mercuric chloride. In every pair of mercuric compounds the mercuric contains *twice* as much complementary radical, in proportion to the mercury, as the mercurous.

Note on Nomenclature.—The remarks made concerning the two classes of iron salts, ferrous and ferric (p. 140), apply in the main to the two series of mercury salts. The latter are systematically distinguished in most modern works by the terms *mercurous* and *mercuric*. In the British and United States Pharmacopœias, however, which include only a few in comparison with the whole number of mercury salts, older and more strongly contrasted names are employed, thus:—

Systematic names.	Official names.
Mercurous iodide	Green iodide of mercury.
Mercuric iodide	Red iodide of mercury.
Mercurous nitrate	Not mentioned.
Mercuric nitrate	Nitrate of mercury.
Mercurous sulphate	Not mentioned.
Mercuric sulphate	Sulphate of mercury.
Mercurous chloride	Subchloride of mercury.
Mercuric chloride	Perchloride of mercury.
Mercurous oxide	Black oxide of mercury.
Mercuric oxide	Red oxide of mercury.

Specific gravity.—Mercury is 13.6 times as heavy as water.

Amalgams.—The compound formed in fusing metals together is usually termed an *alloy* (*ad* and *ligo*, to bind); but if mercury is a constituent, an *amalgam* (*μάλαγμα*, *malagma*, from *μαλάσσω*, *malassō*, to soften, the presence of mercury lowering the melting-point of such a mixture). Most metals, even hydrogen, according to Leow, form amalgams.

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* The specific gravity of the vapor of calomel, and the fact that the salt is *not* decomposed at the temperature at which its specific gravity is taken, indicate that the formula of calomel is HgCl, and not Hg_2Cl_2.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

The Two Iodides.

First Synthetical Reaction.—Rub together a small quantity of mercury and iodine, controlling the rapidity of combination by adding, previously, and afterward occasionally, a few drops of spirit of wine, which, by evaporation, absorbs heat, and thus keeps down temperature. The product is either mercuric iodide, mercurous iodide, or a mixture of the two, as well as mercury or iodine if excess of either has been employed. If the two elements have been previously weighed in single atomic proportions, 200 of mercury to 127 of iodine (about 8 to 5, or 1 ounce of mercury to 278 grains of iodine), the mercurous or green (grayish-green) iodide results (HgI) (*Hydrargyri Iodidum Viride*, U. S. P.); if in the proportion of one atom of mercury to two atoms of iodine (200 to twice 127, or about 4 to 5), the mercuric or red iodide, HgI_2, results, an iodide that is also official, but made in another way. (See page 194.) The green iodide should be made and dried (without heat) with as little exposure to light as possible. The product should be well washed with alcohol to remove mercuric iodide.

Mercurous iodide is decomposed slowly by light, and quickly by heat, into mercuric iodide and mercury. Mercuric iodide occurring as an impurity in mercurous iodide may be detected by digesting in ether (in which mercurous iodide is insoluble), filtering and evaporating to dryness; mercuric iodide remains. Mercuric iodide is stable, and may be sublimed in scarlet crystals without decomposition. (For details of the method by which a specimen of the crystals may be obtained, and the precautions to be observed, *vide* "Corrosive Sublimate," p. 198.)

Relation of Mercuric Iodide to Light.—In condensing, mercuric iodide is at first yellow, afterwards acquiring its characteristic scarlet color. This may be shown by smearing or rubbing a sheet of white paper with the red iodide, and then holding the sheet before a fire or over a flame for a few seconds. As soon as the paper becomes hot the red instantly changes to yellow, and the salt does not quickly regain its red color, even when cold, if the paper is carefully handled. But if a mark be made across the sheet with anything at hand, or the salt be pressed or rubbed in any way, the portions touched immediately return to the scarlet condition. According to Warrington, this change is consequent upon rhomboidal crystals being converted into octahedra with a square base, and will serve as an excellent illustration of the influence of physical structure in causing color. The yellow modification so acts on the rays of white light shining on its particles as to absorb the violet and reflect the complementary hue, the yellow, which, entering the eye of the observer, strikes his retina, and thus conveys to the brain the impression of yellowness; and the red modification, though actually the same chemical substance, is sufficiently different in the structure of its particles to absorb the green constituent of white light and reflect the complementary ray, the red.

Illustration of the Chemical Law of Multiple Proportions (p. 48). —Applying the atomic theory to the above iodides, it will at once be apparent why mercury and iodine should combine in the proportion of 200 of mercury with either 127 or 254 of iodine, and not with any intermediate quantity. For it is part of that theory that masses are composed of atoms, and that atoms are indivisible; and that the weight of the atom of mercury is to that of iodine as 200 is to 127. Mercury and iodine can only combine, therefore, in atomic proportions, atom to atom (which is the same as 200 to 127), or one atom to two atoms (which is the same as 200 to 254). To attempt to combine them in any intermediate proportion would be useless; a mere mixture of the two iodides would result. A higher proportion of mercury than 200 to 127 of iodine gives but a mixture of mercurous iodide and mercury; a higher proportion of iodine than 254 to 200 of mercury gives but a mixture of mercuric iodide and iodine. Or, for example, 200 grains of mercury, mixed with, say, 200 of iodine, would yield 139 grains of mercurous iodide and 261 grains of mercuric iodide; for the 200 grains of mercury uniting with 127 grains of the iodine give, for the moment, 327 grains of mercurous iodide and 73 grains of iodine still free. The 73 grains of iodine will immediately unite with 188 grains of the mercurous iodide (for if 127 of I require 327 of HgI to form HgI_2, 73 will require 188), and form 261 grains of mercuric iodide, diminishing the 327 grains of mercurous iodide to 139 grains.

Preparation of Red Iodide of Mercury by precipitation.—To a few drops of a solution of a mercuric salt (corrosive sublimate, for example), add solution of iodide of potassium, drop by drop; a precipitate of mercuric iodide, HgI_2, forms, and at first quickly redissolves, but is permanent when sufficient iodide of potassium has been added. Continue the addition of iodide of potassium; the precipitate is once more redissolved.

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Iodide of potassium.}}{2KI} = \underset{\text{Mercuric iodide.}}{HgI_2} + \underset{\text{Chloride of potassium.}}{2KCl}$$

Note.—When first precipitated, mercuric iodide is yellowish-red, but soon changes to a beautiful scarlet. Its solubility either in solution of the mercuric salt or in solution of iodide of potassium renders the detection of a small quantity of a mercuric salt by iodide of potassium, or a small quantity of an iodide by a mercuric solution, difficult, and hence lessens the value of the reaction as a test. But the reaction has synthetical interest, the method by precipitation being that adopted in the British and United States Pharmacopœias (*Hydrargyri Iodidum Rubrum*, U. S. P.). Mercuric iodide thus made has the same composition as that prepared by direct combination of its elements. Equivalent proportions of the two salts must be used in making the preparation ($HgCl_2 = 271$; $2KI = 332$). About 4 parts of corrosive sublimate are dissolved in 50 or 60 of water (warmth quickens solution), and 5 of iodide of potassium in 15 or 20 of water, the solutions mixed, and the precipitate collected on a filter, drained, washed twice with distilled water, and dried on a plate over a water-bath. Mercuric nitrate, which is more soluble, and therefore somewhat more convenient for use on the large scale, may be used instead of the mercuric chloride. The mercury in mercuric or mercurous iodide is set free and sublimes in globules on heating either powder with dried carbonate of sodium in a test-tube; the iodine may be detected by digesting with solution of soda, filtering, and to the solution of iodide of sodium thus formed adding starch paste and acidulating with nitrous acid, when blue iodide of starch results. Mercuric iodide is insoluble in water, slightly soluble in alcohol, tolerably soluble in ether. Precipitated red iodide of mercury mixed with white wax, lard, and oil, forms the *Unguentum Hydrargyri Iodidi Rubri*, B. P. 100 parts of a 5-per cent. solution of mercuric chloride with 367 parts of a 5-per cent. solution of iodide of potassium forms the "Test Solution of Iodide of Mercury and Potassium," U. S. P.

The Two Nitrates.

Second Synthetical Reaction.—Place a globule of mercury, about half the size of a pea, in a test-tube; add twenty or thirty drops of nitric acid; boil slowly until red fumes (nitric oxide, NO) no longer form; set aside. On cooling, if a globule of mercury still remains in the tube, crystals of mercurous nitrate separate. These may be dissolved in water slightly acidulated by nitric acid. The solution may be retained for subsequent analytical operations.

$$Hg_3 + 4HNO_3 = 3HgNO_3 + 2H_2O + NO.$$

Third Synthetical Reaction.—Place mercury in *excess* of strong nitric acid, and warm the mixture; mercuric nitrate is formed, and will be deposited in crystals as the solution cools. Or, to crystals of mercurous nitrate add nitric acid and boil until red fumes cease to form. Retain the product for a subsequent experiment.

It will be seen that when mercury and nitric acid are boiled together mercurous nitrate is formed if the mercury be in excess, while mercuric nitrate is produced if the acid preponderate.

The mercuric nitrates vary somewhat in composition, according to the proportion, strength, and temperature of the acid used in their formation. A mercuric nitrate may be obtained having the formula $Hg2NO_3$.

$$\underset{\text{Mercury.}}{Hg_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Mercuric}\\\text{nitrate.}}}{3(Hg2NO_3)} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Mercuric Oxynitrates.—From the normal mercuric nitrate several oxynitrates may be obtained. Thus on merely evaporating a solution of mercuric nitrate, and cooling, crystals having the formula $Hg_6O_36NO_3$ are deposited. The latter, by washing with cold water, yield a *yellow* pulverulent oxynitrate, $Hg_6O_44NO_3$: mixed with lard, this has sometimes been used as an ointment. Boiled in water, the yellow gives a *brick-red* oxynitrate, $Hg_6O_52NO_3$.

The pharmacopœial preparations of mercuric nitrate are *Liquor Hydrargyri Nitratis*, U. S. P., containing half its weight of mercuric nitrate and free acid, sp. gr. 2.100, and *Unguentum Hydrargyri Nitratis*, U. S. P. The former is made by placing 40 parts of red oxide of mercury in 45 parts of nitric acid diluted with 15 parts of water.

$$HgO + 2HNO_3 = Hg2NO_3 + H_2O.$$

The *Unguentum* or "Citrine Ointment" is made by oxidizing lard oil with nitric acid, and then adding a solution of mercury in nitric acid.

The Two Sulphates.

Fourth Synthetical Reaction.—Boil two or three grains of mercury with a few drops of strong sulphuric acid in a test-tube, or, better, small dish; sulphurous acid gas (SO_2) is evolved, and mercuric sulphate (*Hydrargyri Sulphas*, B. P.) ($HgSO_4$) results—a white heavy crystalline powder.

$$\underset{\text{Mercury.}}{Hg} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Mercuric}\\\text{sulphate.}}}{HgSO_4} + \underset{\substack{\text{Sulphurous}\\\text{acid gas.}}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Between two and three ounces of mercuric sulphate may be prepared from a fluidrachm of mercury and a fluidounce of sulphuric acid boiled together in a small dish. These are the official proportions. The operation is completed and any excess of acid removed by evaporating the mixture of metal and liquid to dryness, either in the open air or in a fume-chamber, sulphuric acid vapors being excessively irritating to the mucous membrane of the nose and throat; dry crystalline mercuric sulphate remains. If residual particles of mercury are observed, the mass should be dampened with sulphuric acid and again heated.

By-products.—In chemical manufactories, secondary products, such as the sulphurous gas of the above reaction, are termed *by-products*, and, if of value, are utilized. In the present case the gas is of no immediate use, and is therefore allowed to escape. When very pure sulphurous acid gas is required for experiments on the small scale, this would be the best method of making it, a delivery-tube being adapted by a cork to the mouth of a flask containing the acid and metal. The sulphate of mercury would then become the by-product.

Mercuric Oxysulphate.—Water decomposes mercuric sulphate into a soluble acid salt and an insoluble yellow oxysulphate ($Hg_3O_2SO_4$). The latter is called *Turpeth mineral*, from its resemblance in color to the powdered root of *Ipomœa turpethum*, an Indian substitute for jalap. The yellow sulphate or subsulphate of mercury (*Hydrargyri Subsulphas Flavus*, U. S. P.) is official. It should be entirely soluble in 20 parts of hydrochloric acid.

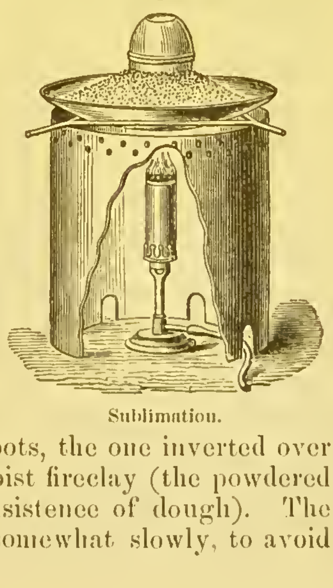
Fifth Synthetical Reaction.—Rub a portion of the dry mercuric sulphate of the previous reaction with as much mercury as it already contains; the product, when the two have thoroughly blended, is mercurous sulphate (Hg_2SO_4): it may be retained for a subsequent experiment.

Molecular Weight.—The exact proportion of mercury to sulphate is merely a matter of calculation; for the combining proportion of a compound (if it possess any combining power) is the sum of the combining proportions of its constituents. *In other words, the combining weight of a molecule is simply the sum of the weights of its constituent atoms*, or, more generally, *the molecular weight of a compound is the sum of the atomic weights of its elements.* In accordance with this rule (sometimes called the fourth law of chemical combination, though only a deduction from the first—p. 47), 296 of mercuric sulphate and 200 of mercury (about 3 to 2) are the exact proportions necessary to the formation of mercurous sulphate.

The Two Chlorides.

Sixth Synthetical Reaction.—Mix thoroughly a few grains of dry mercuric sulphate with about four-fifths its weight of chloride of sodium, and heat the mixture slowly in a test-tube in a fume-chamber or in the open air to leeward of the operator; mercuric chloride ($HgCl_2$), or *corrosive sublimate* (*Hydrargyri Perchloridum*, B. P., *Hydrargyri Chloridum Corrosivum*, U. S. P.), sublimes and condenses in the upper part of the tube in heavy colorless crystals or a crystalline mass. Somewhat larger quantities (in the proportion of 20 of sulphate to 16 of salt, and, *vide infra*, 1 of black oxide of manganese) may be sublimed in a pair of two-ounce or three-ounce round-bottomed gallipots, the one inverted over the other, and the joint luted by moist fireclay (the powdered clay kneaded with water to the consistence of dough). The luting having been allowed to dry (somewhat slowly, to avoid

Fig. 36.



Sublimation.

cracks), the pots are placed upright on a sand-tray (plate-shape answers very well), sand piled round the lower and a portion of the upper pot, and the whole heated over a good-sized gas-flame (if an air-gas flame, it should be an inch and a half wide and four or five inches long) for an hour or more (see fig. 36—pots raised to show joint). Red Iodide of Mercury and Calomel may be sublimed in the same way. The former requires less, the latter more, heat than corrosive sublimate.

$$\underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Chloride of sodium.}}{2NaCl} = \underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4}$$

Note.—If the mercuric sulphate contain any mercurous sulphate, some calomel may be formed. This result will be avoided if 2 or 3 per cent. of black oxide of manganese be previously mixed with the ingredients, the action of which is to eliminate chlorine from the excess of chloride of sodium used in the process, the chlorine converting any calomel into corrosive sublimate. Manganate of sodium and a lower oxide of manganese are simultaneously produced.

Precaution.—The operation is directed to be conducted with care in a fume-chamber or in the open air, because the vapor of corrosive sublimate, which might possibly escape, is very acrid and highly poisonous. Its vulgar name is indicative of its properties.

Ten grains of perchloride of mercury and the same quantity of chloride of ammonium in one pint of water form the *Liquor Hydrargyri Perchloridi*, B. P. A dilute aqueous solution of perchloride of mercury is liable to decomposition, calomel being precipitated, water decomposed, hydrochloric acid formed, and oxygen gas evolved. The presence of excess of chloride of ammonium, with a portion of which the mercuric chloride forms a stable double salt, prevents the decomposition.

Seventh Synthetical Reaction.—Mix a few grains of the mercurous sulphate of the fifth reaction with about a third of its weight of chloride of sodium, and sublime in a test-tube; crystalline mercurous chloride (HgCl) or calomel (*Hydrargyri Subchloridum*, B. P., *Hydrargyri Chloridum Mite*, U. S. P.) results. Larger quantities may be prepared in the manner directed for corrosive sublimate, a somewhat higher temperature being employed; similar precaution must also be observed. The proportions are 10 of mercuric sulphate to 7 of mercury and 5 of dry chloride of sodium. "Moisten the sulphate of mercury with some of the water, and rub it and the mercury together until globules are no longer visible; add the chloride of sodium, and thoroughly mix the whole by continued trituration. When dry, sublime by a suitable apparatus into a chamber of such a size that the calomel, instead of adhering to its sides as a crystalline crust, shall fall as a fine (dull-white) powder on its floor. Wash this powder with boiling distilled water until the washings cease to be darkened by a drop of sulphydrate of ammonium. Finally, dry at a heat not exceeding 212° F., and preserve in a jar or bottle impervious to light."

$$\underset{\text{Mercurous sulphate.}}{Hg_2SO_4} + \underset{\text{Chloride of sodium.}}{2NaCl} = \underset{\text{Mercurous chloride.}}{2HgCl} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4}$$

The term *calomel* (*χαλὸς*, *kalos*, good, and *μέλας*, *melas*, black) is said to relate to the use of the salt as a *good* remedy for *black* bile, but probably was simply indicative of the esteem in which black sulphide of mercury was held, the compound to which the name calomel was first applied.

Test for corrosive sublimate in calomel.—If the mercurous sulphate contains mercuric sulphate, some mercuric chloride will also be formed. Corrosive sublimate is soluble in water, calomel insoluble; the presence of the former may therefore be proved by boiling a few grains of the calomel in distilled water, filtering and testing by sulphuretted hydrogen or sulphydrate of ammonium as described hereafter. If corrosive sublimate is present, the whole bulk of the calomel must be washed with hot distilled water till the filtrate ceases to give any indications of mercury. Corrosive sublimate is more soluble in alcohol, and still more in ether; calomel insoluble. Ether in which calomel has been digested should, therefore, after filtration, yield no residue on evaporation. Calomel is converted by hydrocyanic acid into mercuric salt, and a black powder readily yielding metallic mercury. Powell and Bayne have shown that a certain proportion of hydrochloric acid arrests this action.

Note.—The above process is that of the Pharmacopœia; but calomel may also be made by other methods. Calomel mixed with lard forms the *Unguentum Hydrargyri Subchloridi*, B. P., with sulphurated antimony, guaiacum resin, and mucilage of tragacanth the *Pilulæ Antimonii Compositæ*, U. S. P., or "Plummer's Pills," and with colocynth, jalap, and gamboge the *Pilulæ Catharticæ Compositæ*, U. S. P.

The Two Oxides.

Eighth Synthetical Reaction.—Evaporate the mercuric nitrate of the third reaction to dryness in a small dish in a fume-chamber, or in the open air if more than a few grains have been prepared, and heat the residue till no more fumes are evolved; red mercuric oxide (HgO), "Red Precipitate," the Red Oxide of Mercury (*Hydrargyri Oxidum Rubrum*, U. S. P.), remains.

$$\underset{\text{Mercuric nitrate.}}{2(Hg2NO_3)} = \underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Nitric peroxide.}}{4NO_2} + \underset{\text{Oxygen.}}{O_2}$$

The nitric constituents of the salt may be partially economized by previously thoroughly mixing with the dry mercuric nitrate as much mercury as is used in its preparation, or as much as it already contains (ascertained by calculation from the atomic weights and the weight of nitrate under operation, as in making mercurous sulphate p. 197), and well heating the mixture. In this case the free mercury is also converted into mercuric oxide. This is the official process, the Pharmacopœial quantities being four ounces of mercury dissolved in four and a half fluidounces of nitric acid diluted with two ounces of water, the solution evaporated to dryness, the residue thoroughly mixed with four ounces of mercury, and the whole heated until acid vapors cease to be evolved. (Mercuric oxide is tested for nitrate by heating a little of the sample in a test-tube, when orange nitrous vapors are produced and are visible in the upper part of the tube, if nitrate is present.)

$$\underset{\substack{\text{Mercuric}\\ \text{nitrate.}}}{Hg2NO_3} + \underset{\text{Mercury.}}{Hg} = \underset{\substack{\text{Mercuric}\\ \text{oxide.}}}{2HgO} + \underset{\substack{\text{Nitric}\\ \text{peroxide.}}}{2NO_2}$$

Mercuric oxide is an orange-red powder, more or less crystalline according to the extent to which it may have been stirred during preparation from the nitrate, much rubbing giving the crystals a pulverulent character. Mercuric oxide, in contact with oxidizable organic matter, is liable to reduction to black or mercurous oxide.

Ninth Synthetical Reaction.—To solution of *potash* or soda, or lime-water, in a test-tube or larger vessel, add solution of corrosive sublimate or of mercuric nitrate; yellow oxide of mercury (*Hydrargyri Oxidum Flavum*, U. S. P.), or yellow mercuric oxide (HgO), is precipitated.

$$\underset{\substack{\text{Mercuric}\\ \text{chloride.}}}{HgCl_2} + \underset{\substack{\text{Hydrate of}\\ \text{potassium.}}}{2KHO} = \underset{\substack{\text{Mercuric}\\ \text{oxide.}}}{HgO} + \underset{\substack{\text{Chloride of}\\ \text{potassium.}}}{2KCl} + \underset{\text{Water.}}{H_2O}$$

The precipitate only differs physically from the red mercuric oxide; the yellow is in a more minute state of division than the red. Mercuric oxide is very slightly soluble in water, but sufficiently so to communicate a decidedly metallic taste.

Tenth Synthetical Reaction.—To calomel add solution of potash or soda, or lime-water; black oxide of mercury, or mercurous oxide (Hg_2O) is produced, and may be filtered off, washed, and dried. (This reaction and the formation of a white curdy precipitate, on the addition of solution of nitrate of silver to the filtrate from the mercurous oxide, acidified by nitric acid, form sufficient evidence of a powder being or containing calomel. The curdy precipitate is chloride of silver.)

Thirty grains of calomel to ten ounces of lime-water form the *Lotio Hydrargyri Nigra*, B. P.

$$\underset{\substack{\text{Mercurous}\\ \text{chloride.}}}{2HgCl} + \underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Mercurous}\\ \text{oxide.}}}{Hg_2O} + \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

(*b*) *Analytical Reactions* (*Tests*).

(The mercury occurring as mercuric or mercurous salts.)

First Analytical Reaction.—The Copper Test. Deposition of mercury upon, and sublimation from copper.—Place a small piece of bright copper, about half an inch long and a quarter of an inch broad, in a solution of any salt of mercury, mercurous or mercuric, and heat in a test-tube; the copper becomes coated with mercury in a fine state of division. (The absence of any notable quantity of nitric acid must be insured or the copper itself will be dissolved. See notes below.) Pour away the supernatant liquid from the copper, wash the latter once or twice by pouring water into, and then out of, the tube, remove the metal, take off excess of water by gentle pressure in a piece of filter-paper, dry the copper by passing it quickly through a flame, holding it by the fingers; finally, place the copper in a dry narrow test-tube, and heat to redness in a flame, the tube being held almost horizontally; the mercury sublimes and condenses as a whitish sublimate of minute globules on the cool part of the tube outside the flame. The globules aggregate on gently pressing with a glass rod, and are especially visible where flattened between the rod and the side of the test-tube.

Notes on the Test.—This is a valuable test, for several reasons: It is very delicate when performed with care. It brings before the observer the element itself—one which from its metallic lustre and fluidity cannot be mistaken for any other. It separates the element both from mercurous and mercuric salts. Mercury can in this way readily be eliminated in the presence of most other substances, organic or inorganic.

In performing the test the presence of any quantity of nitric acid may be avoided by adding an alkali until a slight permanent precipitate appears, and then reacidifying with a few drops of acetic or hydrochloric acid; or by concentrating in an evaporating-dish after adding a little sulphuric acid, and then rediluting.

Tests continued. (The mercury occurring as mercuric salt.)

Second Analytical Reaction.—To a few drops of a solution of a mercuric salt (corrosive sublimate, for example) add solution of iodide of potassium, drop by drop; a precipitate of mercuric iodide (HgI_2) forms, and at first quickly redissolves, but is permanent when sufficient iodide of potassium has been added. Continue the addition of iodide of potassium; the precipitate is once more redissolved.

Third Analytical Reaction.—Add a solution of mercuric salt to solution of ammonia, taking care that the mixture, after well stirring, still smells of ammonia; a white precipitate falls.

Ammoniated Mercury.

Performed in a test-tube, this reaction is a very delicate test of the presence of a mercuric salt; performed in larger vessels, the mercuric salt being corrosive sublimate (3 ounces dissolved in 3 pints of distilled water, the solution poured into 4 fluidounces of Solution of Ammonia, and the precipitate washed and dried over a water-bath), it is the usual process for the preparation of "white precipitate," the old "ammonio-chloride," or "amido-chloride of mercury" (so called because then considered to be a compound of mercury with chlorine and with *amidogen*, NH_2, or $HgCl_2, Hg2NH_2$, chloride and *amide* of mercury), now known as Ammoniated Mercury (*Hydrargyrum Ammoniatum*, U. S. P.).

Constitution of Ammoniated Mercury.—This precipitate is considered to be the chloride of mercuric ammonium ($NH_2Hg''Cl$)—that is, chloride of ammonium (NH_4Cl), in which two univalent atoms of hydrogen are replaced by one bivalent atom of mercury.

$$\underset{\substack{\text{Mercuric}\\\text{chloride.}}}{HgCl_2} + \underset{\text{Ammonia.}}{2NH_4HO} = \underset{\substack{\text{"White}\\\text{precipitate."}}}{NH_2Hg''Cl} + \underset{\substack{\text{Chloride of}\\\text{ammonium.}}}{NH_4Cl} + \underset{\text{Water.}}{2H_2O}$$

Varieties of Ammoniated Mercury.—If the order of mixing be reversed, and ammonia be added to solution of mercuric chloride, a double chloride of mercuric-ammonium and mercury results ($NH_2HgCl,HgCl_2$): it contains 76.55 per cent. of mercury. Previously to the year 1826, "white precipitate" was officially made by adding a fixed alkali to a solution of equal parts of corrosive sublimate and sal-ammoniac; this gave a double chloride of mercuric ammonium and ammonium (NH_2HgCl,NH_4Cl), containing 65.57 per cent. of mercury. This compound is now known as "*fusible* white precipitate," because at a temperature somewhat below redness it fuses and then volatilizes. The "white precipitate" which has been official since 1826 contains 79.52 per cent. of mercury. The true compound may be distinguished as "*infusible* white precipitate," from the fact that when heated it volatilizes without fusing. An ointment of this body is official (*Unguentum Hydrargyri Ammoniati*, U. S. P.). Prolonged washing with water converts "white precipitate" into a yellowish compound (NH_2HgCl,HgO); hence the official preparation is seldom thoroughly freed from the chloride of ammonium which is formed during its manufacture, and which, if present in larger proportion than seven or eight per cent., gives to it the character of partial or complete fusibility. With iodine, chlorine, or bromine, white precipitate may yield the highly explosive iodide, chloride, or bromide of nitrogen.

Note.—Chloride of mercuric-ammonium is only one member of a large class of compounds derivable from the various salts of ammonium by displacement of atoms of hydrogen in the molecules by other atoms. The composition of the chloride of mercurous-ammonium (see next page) and of ammonio-nitrate of silver is consistent with this view.

$N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right\}Cl$	$N\left\{\begin{matrix}Hg'\\Hg'\\H\\H\end{matrix}\right\}Cl$	$N\left\{\begin{matrix}Hg''\\H\\H\end{matrix}\right\}Cl$	$N\left\{\begin{matrix}Ag\\Am\\H\\H\end{matrix}\right\}NO_3$
Chloride of common ammonium.	Chloride of mercurous-ammonium.	Chloride of mercuric-ammonium.	Nitrate of argent-ammon-ammonium.

The composition of the ammonio-sulphates of copper (pp. 173 and 189) is consistent with the second and third of the following formulæ, the first being that of sulphate of ammonium:—

$$N_2\left\{\begin{matrix}H_2\\H_2\\H_2\\H_2\end{matrix}\right\}SO_4 \quad\Bigg|\quad N_2\left\{\begin{matrix}Cu''\\Am_2\\H_2\\H_2\end{matrix}\right\}SO_4 \quad\Bigg|\quad N_2\left\{\begin{matrix}Cu''\\Am_2\\Am_2\\H_2\end{matrix}\right\}SO_4$$

The iodide of dimercuric ammonium (NHg''_2I) is formed in testing for ammonia by the "Nessler" reagent (*vide* Index). Troost has obtained $NHAm_3Cl$.

Fourth Analytical Reaction.—Pass sulphuretted hydrogen through a mercuric solution; a black precipitate of mercuric sulphide (HgS) falls.

Note.—Sulphuretted hydrogen also precipitates mercurous sulphide (Hg_2S) from mercurous solutions; and in appearance the precipitates are alike; hence this reagent does not distinguish between mercurous and mercuric salts. But in the course of systematic analysis, mercuric salts are thrown down from solution as sulphide after mercurous salts have been otherwise removed. The sulphides are insoluble in sulphydrate of ammonium.

Note.—An insufficient amount of the gas gives a white or colored precipitate of oxysulphide. Prolonged contact with sulphuretted hydrogen-water or a sulphydrate, especially when the mixture is kept warm, converts the black into a red sulphide.

Æthiops Mineral, the *Hydrargyri Sulphuretum cum Sulphure*, is a mixture of sulphide of mercury and sulphur, obtained on triturating the elements in a mortar till globules are no longer visible. Its name is probably in allusion to its similarity in color to the skin of the Æthiop. It was formerly official.

Vermilion or *artificial cinnabar*, is mercuric sulphide prepared by sublimation (*Hydrargyri Sulphidum Rubrum*, U. S. P.). For a description of the Chinese method of manufacturing it see the *Pharmaceutical Journal* for December 17, 1881.

Tests continued. (The mercury occurring as mercurous salt.)

Fifth Analytical Reaction.—To a solution of a mercurous salt (the mercurous nitrate obtained in the second synthetical reaction, for example) add hydrochloric acid or any soluble chloride; a white precipitate of calomel (HgCl) occurs.

This reaction was formerly official in the Dublin Pharmacopœia as a process for the preparation of calomel.

Sixth Analytical Reaction.—To solution of a mercurous salt add iodide of potassium; green mercurous iodide (HgI) is precipitated.

Seventh Analytical Reaction.—To a mercurous salt, dissolved or undissolved (*e. g.* calomel), add ammonia; black salt (*e. g.* chloride) of mercurous ammonium NH_2Hg_2Cl) is formed (see previous page).

Other Tests for Mercury.

The elimination of mercury in the actual state of metal by the copper test, coupled with the production or non-production of a white precipitate on the addition of hydrochloric acid to the original solution, is usually sufficient evidence of the presence of mercury and its existence as a mercurous or mercuric salt. But other tests may sometimes be applied with advantage. Thus, metallic mercury is deposited on placing a drop of the solution on a plate of gold (sovereign or half sovereign), and touching the drop and the edge of the plate simultaneously with a key; an electric current passes, under these circumstances, from the gold to the key, and thence through the liquid to the gold, decomposing the salt, the mercury of which forms a white metallic spot on the gold, while the other elements go to the iron. This is called *the galvanic test*, and is useful for clinical purposes.——Solution of stannous chloride ($SnCl_2$)—see Index—from the readiness with which it forms stannic salts ($SnCl_4$, SnO_2, etc.), gives a white precipitate of mercurous chloride in mercuric solutions, and quickly still further reduces this mercurous chloride (and other mercury-salts) to a grayish mass of finely divided mercury; this is the old *magpie test*, probably so called from the white and gray appearance of the precipitate. The reaction may even be obtained from such insoluble mercury compounds as "white precipitate."——Confirmatory tests for mercuric and mercurous salts will be found in the action of solution of potash, solution of soda, lime-water, solution of ammonia, and solution of iodide of potassium. (*Vide* pages 201 to 204.)——Normal alkaline carbonates produce yellowish mercurous carbonate and brownish-red mercuric carbonate, both of them unstable.——Alkaline bicarbonates give mercurous carbonate with mercurous salts, and with mercuric salts white (becoming red) mercuric oxysalt.——Yellow chromate of potassium (K_2CrO_4) gives with mercurous salts, a red precipitate of mercurous chromate (Hg_2CrO_4).——Mercury and all its compounds are volatile, many of them being decomposed, at the same time yielding globules of condensed metal: the experiment is most conveniently performed in a test-tube.——All dry compounds of mercury are decomposed when heated in a dry test-tube with dried carbonate of sodium, mercury subliming and condensing in visible globules or as a whitish deposit yielding globules when rubbed with a glass rod.

Antidote.—Albumen gives a white precipitate with solution of mercuric salts; hence the importance of administering white of egg while waiting for a stomach-pump in cases of poisoning by corrosive sublimate.

QUESTIONS AND EXERCISES.

293. Name the chief ore of mercury, and describe a process for the extraction of the metal.

294. Give the properties of mercury.

295. In what state does mercury exist in "Gray Powder"?

296. What other preparations of metallic mercury itself are employed in medicine?

297. State the relation of the mercurous to the mercuric compounds.

298. Distinguish between an *alloy* and an *amalgam.*

299. State the formulæ of the two Iodides of Mercury.

300. Under what circumstances does mercuric iodide assume two different colors?

301. Illustrate the chemical law of Multiple Proportions as explained by the atomic theory, employing for that purpose the stated composition of the two iodides of mercury.

302. Write down the formulæ of Mercurous and Mercuric Nitrates and Sulphates.

303. How is Mercuric Sulphate prepared?

304. What is the formula of "Turpeth Mineral"?

305. Describe the processes necessary for the conversion of mercury into Calomel and Corrosive Sublimate, using diagrams.

306. Why is black oxide of manganese sometimes mixed with the other ingredients in the preparation of Corrosive Sublimate?

307. Give the chemical and physical points of difference between Calomel and Corrosive Sublimate.

308. How may a small quantity of Calomel in Corrosive Sublimate be detected?

309. Work out a sum showing how much mercury will be required in the manufacture of one ton of Calomel. *Ans.* 17 cwt. nearly.

310. Mention official preparations of the chlorides of mercury.

311. Give the formulæ and mode of formation of the Red, Yellow, and Black Oxides of Mercury, employing diagrams.

312. Explain the action of the chief general test for mercury.

313. How are mercurous and mercuric salts analytically distinguished?

314. Give a probable view of the constitution of *Hydrargyrum Ammoniatum*, and an equation showing how it is made.

315. What is the best temporary antidote in cases of poisoning by mercury?

LEAD.

Symbol Pb. Atomic weight 206.5.

Source.—The ores of lead are numerous; but the one form which the metal is chiefly obtained is the sulphide of lead (PbS), or *galena* (from γαλήνη, *galene*, tranquillity, perhaps from its supposed effect in allaying pain).

Preparation.—The ore is first roasted in a current of air; much sulphur is thus burnt off as sulphurous acid gas, while some of the metal is converted into oxide and a portion of the sulphide oxidized to sulphate. Oxidization being stopped when the mass presents certain appearances, the temperature is raised, and the oxide and sulphate, reacting on undecomposed sulphide, yield the metal and much sulphurous acid gas:—

$$2PbO + PbS = Pb_3 + SO_2$$
$$PbSO_4 + PbS = Pb_2 + 2SO_2.$$

Uses.—The uses of lead are well known. Alloyed with arsenicum it forms common *shot*, with antimony gives *type-metal*, with tin *solder*, and in smaller quantities enters into the composition of *Britannia metal*, *pewter*, and other alloys. Lead is so slightly attacked by acids that chemical vessels and instruments are often made of it. Even hot hydrochloric acid only slowly converts it into chloride of lead, with evolution of hydrogen. Sulphuric acid by aid of air only very slowly attacks it, with formation of sulphate of lead and water. Even nitric acid very slowly converts it into nitrate, with evolution of nitric oxide and nitrous oxide gases and water.

The salts of lead used in pharmacy and all other preparations of lead are obtained, directly or indirectly, from the metal itself. Heated in a current of air, lead combines with oxygen and forms oxide of lead (PbO) (*Plumbi Oxidum*, U. S. P.), a yellowish powder (*massicot*), or if fused and solidified a brighter reddish-yellow heavy mass of bright scales, termed *litharge* (from λίθος, *lithos*, a stone, and ἀργυρος, *arguros*, silver). It is from this oxide that the chief lead compounds are obtained. Oxide of lead, by further roasting in a current of air, yields *red lead* (or *minium*), Pb_3O_4, or $PbO_2{,}2PbO$. Both oxides are much used by painters, paper-stainers, and glass-manufacturers. *White lead* is a mixture of carbonate ($PbCO_3$) and hydrate of lead ($Pb2HO$) (commonly 2 molecules of the former to 1 of the latter), usually ground up with about 7 per cent. of linseed oil; it is made by exposing lead, cast in spirals or little gratings, to the action of air, acetic fumes, and carbonic acid, the latter generated from decaying vegetable matter, such as spent tan; oxyacetate of lead slowly but continuously forms, and is as continuously decomposed by the carbonic acid, with production of hydrate and carbonate, or *dry white lead.* The grating-like masses, when ground, form the heavy white pulverulent official *Plumbi Carbonas*, U. S. P. The latter is the active constituent of *Unguentum Plumbi Carbonatis*, U. S. P., the old *Unguentum Cerussæ.*

Lead compounds are poisonous, producing saturnine colic, or even paralysis. These effects are termed *saturnine* from an old name of lead, *Saturn.* The alchemists called lead Saturn, first, because they thought it the oldest of the seven then known metals, and it might therefore be compared to Saturn, who was supposed to be the father of the gods; and, secondly, because its power of dissolving other metals recalled a peculiarity of Saturn, who was said to be in the habit of devouring his own children.

Quantivalence.—The atom of lead is sometimes quadrivalent (Pb''''); but in most of the compounds used in medicine it exerts bivalent activity only (Pb'').

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

Acetate of Lead.

First Synthetical Reaction.—Place a few grains of oxide of lead in a test-tube, add about an equal weight of water and two and a half times its weight of acetic acid, and boil; the oxide dissolves (or, rather, disappears—dissolves with simultaneous decomposition) and forms a solution of acetate of lead ($Pb2C_2H_3O_2$). When cold, or on evaporation if much water has been used (the solution being kept faintly acid), crystals of acetate of lead ($Pb2C_2H_3O_2,3H_2O$) are deposited. Larger quantities are obtained by the same method.

$$\underset{\text{Oxide of lead.}}{PbO} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of lead.}}{Pb2C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

This is the official *Plumbi Acetas*, U. S. P. The salt is termed *Sugar of Lead*, from its sweet taste. Besides its direct use in Pharmacy, it forms three-fourths of the *Pilula Plumbi cum Opio*, B. P.

Subacetate or Oxyacetate of Lead.

Second Synthetical Reaction.—Boil acetate of lead with about four times its weight of water, and rather more than two-thirds its weight of oxide of lead; the resulting filtered liquid is solution of oxyacetate of lead, *Liquor Plumbi Subacetatis*, U. S. P.

The official *Liquor* is made by boiling 170 parts of acetate and 120 of oxide in 800 of distilled water for half an hour (constantly stirring), filtering, and making up for any loss during evaporation by diluting the filtrate with boiled and cooled distilled water until it weighs 1000 parts. Sp. gr. 1.228.

A similar solution was used by M. Goulard, who called it *Extractum Saturni*, and drew attention to it in 1770. It is now frequently termed *Goulard's Extract.* A more dilute solution, 3 of *Liquor* and 97 of boiled and cooled *distilled* water, is also official in the Pharmaeopœia, under the name of *Liquor Plumbi Subacetatis Dilutus.* The latter is commonly known as *Goulard Water* or "Lead Water." The stronger solution is the chief ingredient in *Ceratum Plumbi Subacetatis*, U. S. P., a slight modification of the old *Goulard's Cerate.*

Oxyacetates of Lead.—The official subacetate of lead is not a definite chemical salt. It is probably a mixture of two subacetates of lead, which are well-known crystalline compounds, and which the author is disposed to regard as having a constitution similar to that he has already indicated for some other salts (see Iron and Antimony, also Bismuth). Exposed to air it absorbs carbonic acid gas, and hydrato-carbonate of lead is deposited.

	Acetate of Lead (3 molecules) . .	$Pb_3\ 6C_2H_3O_2$
U. S. P.	Pyro-oxyacetate of lead	$Pb_3O4C_2H_3O_2$
	Goulard's oxyacetate of lead . . .	$Pb_3O_22C_2H_3O_2$
	Oxide of lead (3 molecules) . . .	Pb_3O_3.

$$\underset{\text{Oxide of lead.}}{PbO} + \underset{\text{Acetate of lead.}}{Pb2C_2H_3O_2} = \underset{\text{Official "subacetate."}}{Pb_2O2C_2H_3O_2}$$

$$\text{or } \underset{\text{Oxide of lead.}}{3PbO} + \underset{\text{Acetate of lead.}}{3(Pb2C_2H_3O_2)} = \underbrace{\underset{\text{Pyro-oxyacetate.}}{Pb_3O4C_2H_3O_2} + \underset{\text{Goulard's oxyacetate.}}{Pb_3O_22C_2H_3O_2}}_{\text{The official "subacetate."}}$$

Nitrate of Lead. Red Lead. Peroxide of Lead.

Third Synthetical Reaction.—Digest a few grains of red lead in nitric acid and water; nitrate of lead ($Pb2NO_3$) is formed, and remains in solution, while a puce-colored peroxide of lead (PbO_2) is precipitated.

Nitrate of Lead (*Plumbi Nitras*, U. S. P.) is more directly made by dissolving litharge (PbO) in nitric acid—

$$PbO + 2HNO_3 = Pb2NO_3 + H_2O;$$

but the former reaction serves to bring before the reader two other oxides of lead, namely, red lead (Pb_3O_4) and peroxide of lead (PbO_2). In the latter oxide the quadrivalent character of lead is obvious. Nitrate of lead is used officially in preparing iodide of lead; for this purpose the above mixture is filtered, the precipitate of peroxide of lead purified from adhering nitrate by passing hot water through the filter, the filtrate and washings evaporated to dryness to remove excess of nitric acid, the residual nitrate of lead redissolved by ebullition with a small quantity of hot water, and the solution set aside to crystallize, or a portion at once used for the following experiment. Nitrate of lead forms white crystals derived from octahedra.

Peroxide of lead dissolved in strong hydrochloric acid apparently yields an unstable perchloride ($PbCl_4$).

Iodide of Lead.

Fourth Synthetical Reaction.—To a neutral solution of nitrate of lead add solution of iodide of potassium; a precipitate of iodide of lead (PbI_2) falls (*Plumbi Iodidum*, U. S. P.). It is soluble in solution of chloride of ammonium. Equal weights of the salts may be used in making large quantities.

$$\underset{\text{Nitrate of lead.}}{Pb2NO_3} + \underset{\text{Iodide of potassium.}}{2KI} = \underset{\text{Iodide of lead.}}{PbI_2} + \underset{\text{Nitrate of potassium.}}{2KNO_3}$$

Crystals of Iodide of Lead.—Heat the iodide of lead with the supernatant liquid, and if necessary filter; the salt is dissolved, and again separates in golden crystalline scales as the solution cools.

Oleate of Lead (Lead Plaster).

Fifth Synthetical Reaction.—Boil together in a small dish some very finely-powdered oxide of lead, with nearly twice its weight of olive oil, and ten or twenty times as much water, well stirring the mixture, and from time to time replacing water that has evaporated; the product is a white mass of oleate of lead ($Pb2C_{18}H_{33}O_2$), glycerin remaining in solution in the water. Larger quantities are prepared in the same manner.

$$\underset{\text{Oxide of lead.}}{3PbO} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Oleate of glyceryl (olive-oil or oleine).}}{2(C_3H_5 3C_{18}H_{33}O_2)}$$

$$\underset{\text{Oleate of lead (lead plaster).}}{3(Pb2C_{18}H_{33}O_2)} + \underset{\text{Hydrate of glyceryl (glycerin).}}{2(C_3H_5 3HO)}$$

The action between the oxide of lead and olive oil is slow, requiring several hours for its completion.

The glycerin may be obtained by treating the aqueous product of the above reaction with sulphuretted hydrogen to remove a trace of lead, then digesting with animal charcoal, filtering and evaporating. But on the large scale glycerin is produced as a by-product in the manufacture of candles, for its elements are found in nearly all vegetable and animal fats. (*Vide* Index.) If in making lead plaster the mixture be evaporated to dryness (*Emplastrum Plumbi*, U. S. P.), some of the glycerin will escape with the steam and some remain with the plaster.

Modes of forming *chloride, sulphide, chromate, sulphate, hydrate,* and other salts of lead are incidentally described in the following analytical paragraphs.

(*b*) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—To a solution of lead salt (acetate, for example) add hydrochloric acid; a white precipitate of chloride of lead ($PbCl_2$) is obtained. Boil the precipitate with much water; it dissolves, but, on the solution cooling, is redeposited in small acicular crystals. Filter the cold solution, and pass sulphuretted hydrogen through it; a black precipitate (sulphide of lead, PbS) shows that the chloride of lead is soluble to a slight extent in cold water.

Note.—A white precipitate on the addition of hydrochloric acid, soluble in hot water, and blackened by sulphuretted hydrogen, sufficiently distinguishes lead salts from those of other metals, but the non-production of such a precipitate does not prove the absence of a small quantity of lead, chloride of lead being slightly soluble in cold water. Hydrochloric acid will be found to be a useful but not a delicate test for lead.

Second Analytical Reaction.—Through a dilute solution of a lead salt acidulated with hydrochloric acid pass sulphuretted hydrogen; a black precipitate of sulphide of lead (PbS) occurs.

Lead in Water.—The foregoing is a very delicate test. Should a trace of lead be present in water used for drinking purposes, sulphuretted hydrogen will detect it. On passing the gas through a pint of such acidulated water, a brownish color is produced. If the tint is scarcely perceptible, set the liquid aside for a day; the gas will become decomposed and a thin layer of sulphur be found at the bottom of the vessel, white if no lead be present, but more or less brown if it contain sulphide of lead.

Third Analytical Reaction.—To solution of a lead salt add sulphydrate of ammonium; a black precipitate of sulphide of lead falls, insoluble in excess.

Fourth Analytical Reaction.—To solution of a lead salt add solution of chromate of potassium (K_2CrO_4); a yellow precipitate of chromate of lead ($PbCrO_4$) is formed, insoluble in weak acids or in solution of chloride of ammonium.

Chromes.—This reaction has technical as well as analytical interest. The precipitate is the common pigment termed *chrome yellow* or *lemon chrome.* Boiled with lime and water, a portion of the chromic radical is removed as soluble chromate of calcium, and an oxychromate of lead, of a bright red or orange color (*orange chrome*), is produced.

Fifth Analytical Reaction.—To solution of a lead salt add dilute sulphuric acid, or a solution of a sulphate; a white precipitate of sulphate of lead ($PbSO_4$) falls.

Sulphate of lead is slightly soluble in strong acids, and in solutions of alkaline salts; it is insoluble in acetic acid. It is readily dissolved and indeed decomposed by solution of acetate of ammonium, the liquid yielding the ordinary reactions with soluble chromates and iodides.

In dilute solutions the above sulphuric reaction does not take place immediately; the precipitate, however, falls after a time; its appearance may be hastened by evaporating the mixture nearly to dryness and then rediluting.

The white precipitate always noticed in the vessels in which diluted sulphuric acid is kept is sulphate of lead, derived from the leaden chambers in which the acid is made; solubility in strong acid and insolubility in weak explains its appearance.

Antidotes.—From the insolubility of sulphate of lead in water, the best *antidote*, in a case of poisoning by the acetate or other soluble salt of lead, is a soluble sulphate, such as Epsom salt, sulphate of sodium or alum, vomiting being also induced, or the stomach-pump applied as quickly as possible.

Other tests for lead will be found in the reaction with *iodide of potassium* (*vide* p. 209); with *alkaline carbonates*, a white precipitate ($2PbCO_3 + Pb2HO$) insoluble in excess; with *alkalies*, a white precipitate ($Pb2HO$) more or less soluble in excess; with alkaline *phosphates*, *arseniates*, *ferrocyanides*, and *cyanides*, precipitates mostly insoluble, but of no special analytical interest. Insoluble salts of lead are decomposed by solutions of potash (KHO) or soda ($NaHO$).

The metal is precipitated in a beautifully crystalline state by metallic zinc and some other metals; the *lead tree* is thus formed.——The *blowpipe-flame* decomposes solid lead compounds placed in a small cavity in a piece of charcoal, a soft malleable bead of metal being produced, and a yellowish ring of oxide deposited on the charcoal.

QUESTIONS AND EXERCISES.

316. Write down equations descriptive of the smelting of galena.
317. Mention some of the alloys of lead.
318. How is litharge produced?
319. Give the formulæ of white lead and red lead.
320. Describe the manufacture of white lead.
321. What is the quantivalence of lead?
322. Draw a diagram expressive of the formation of ordinary Acetate of Lead.
323. Describe the preparation and composition of *Liquor Plumbi Subacetatis*.

324. What is the action of nitric acid on red lead, litharge, and metallic lead?

325. How is the official Iodide of Lead prepared?

326. Describe the reaction between oxide of lead, water, and olive oil, at the temperature of boiling water, and give chemical formulæ explanatory of the constitution of the products.

327. Mention the chief tests for lead.

328. How would you search for lead in potable water?

329. What is the composition of chrome yellow?

330. State a method whereby lead, barium, and silver may be separated from each other.

331. Name the best antidote in case of poisoning by the soluble salts of lead.

SILVER.

Symbol Ag. Atomic weight 107.7.

Source.—This element occurs in nature in the free state and as ore, the common variety of the latter being sulphide of silver (Ag_2S) in combination with much sulphide of lead, forming *argentiferous galena.*

Preparation.—The lead from such galena (p. 206) is melted and slowly cooled; crystals of lead separate and are raked out from the still fluid mass, and thus an alloy very rich in silver is finally obtained: this is roasted in a current of air, whereby the lead is oxidized and removed as litharge, pure silver remaining. Other ores undergo various preparatory treatments according to their nature, and are then shaken with mercury, which amalgamates with and dissolves the particles of silver, the mercury being subsequently removed from the amalgam by distillation. Soils and minerals containing metallic silver are also treated in this way. An important improvement in the amalgamation process, by which the mercury more readily unites with the silver, consists in the addition of a small proportion of sodium to the mercury—a discovery simultaneously made in England by Crookes, and in New York by Wurtz. Silver is not readily affected by the weak acids or other fluids of food, though it is rapidly tarnished by sulphur or sulphur compounds. It does not perceptibly attack hydrochloric acid; reduces strong nitric acid to nitrous anhydride (N_2O_3). and a weaker acid to nitric oxide (NO); it reduces hot sulphuric acid to sulphurous anhydride (SO_2), sulphate of silver (Ag_2SO_4) being formed. The latter salt is crystalline and slightly soluble in water.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reaction.*

Impure Nitrate of Silver.

First Synthetical Reaction.—Dissolve a silver coin in nitric acid; nitric oxide gas (NO) and nitrous anhydride (N_2O_3) are evolved, and a solution of nitrates of silver and copper is obtained.

Silver Coinage.—Pure silver is too soft for use as coin; it is therefore hardened by alloying with copper. The silver money of England contains 7.5, of Prussia 25, and of France 10 and 16.5 per cent. of copper; for the fineness of the French standard silver is 0.900 in the five-franc piece, while an inferior alloy of 0.835 is used for the lower denominations. The single-franc piece, composed of the latter alloy, is still made to weigh five grammes, the weight originally chosen for the franc as the unit of the monetary scale when the fineness of the coin was 0.900. It has now become a token, like the British shilling, of which the nominal value exceeds the metallic value. One pound troy of British standard silver is coined into 66 shillings, of which the metal is worth from 60*s*. to 62*s*. according to the market price of silver. The standard fineness of this silver is 0.925, three alloy in 40. British silver coins are a legal tender in payments to the amount of 40*s*. only.

Chloride of Silver.

Second Synthetical Reaction.—To the product of the foregoing reaction add water and hydrochloric acid or a soluble chloride; white chloride of silver (AgCl) is precipitated, copper still remaining in solution. Collect the precipitate on a filter, and wash with water; it is pure chloride of silver.

Note.—The nitrates of silver and copper may also be separated by evaporating the solution of the metals in nitric acid to dryness, and gently heating the residue, when the nitrate of copper is decomposed, but the nitrate of silver is unaffected. The latter may be dissolved from the residual oxide of copper by water.

Chloride of silver may be obtained in crystals by evaporation of its solution in ammonia.

Pure Silver.

Third Synthetical Reaction.—Place the chloride of silver of the previous reaction in a dish, wet it with dilute sulphuric acid, and float a piece of sheet zinc on the mixture; metallic silver is precipitated, and after about one day wholly removed from solution. Collect the precipitate on a filter and wash with water; it is pure metallic silver, and is readily fusible into a single button.

Note.—Any considerable quantity of chloride of silver may also be reduced to the metallic state by fusion, in a crucible, with about half its weight of carbonate of sodium.

Pure Nitrate of Silver.

Fourth Synthetical Reaction.—Dissolve the pure silver of the previous reaction in nitric acid (3 of silver require about 2 or

2½ of strong acid diluted with 5 of water), and remove excess of acid by evaporating the solution to dryness, slightly heating the residue; the product is pure nitrate of silver. Dissolve by heating with a small quantity of water; on the solution cooling, or on evaporation, colorless tabular crystals of nitrate of silver are obtained.

$$\underset{\text{Silver.}}{3Ag_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\substack{\text{Nitric}\\\text{oxide.}}}{2NO} + \underset{\substack{\text{Nitrate of}\\\text{silver.}}}{6AgNO_3} + \underset{\text{Water.}}{4H_2O}$$

Notes.—The solution of pure or refined silver (*Argentum Purificatum*, B. P.) in nitric acid, evaporation, and crystallization constitutes the usual process for the preparation of the nitrate (*Argenti Nitras*, U. S. P.). The salt fused with 4 per cent. of hydrochloric acid (yielding about 5 per cent. of interlacing chloride of silver), and poured into proper moulds, yields the white cylindrical sticks or rods (*Argenti Nitras Fusus*, U. S. P.) commonly termed *caustic* (from *καίω*, *kaio*, I burn), or *lunar caustic*. (The alchemists called silver *Diana* or *Luna*, from its supposed mysterious connection with the moon.) These "caustic points" commonly contain nitrate of potassium, which imparts toughness, the *Argenti Nitras Dilutus*, U. S. P., being formed of equal weights of the salts. The specimen of nitrate of silver obtained in the above reaction, dissolved in water, will be found useful as an analytical reagent. Nitrate of silver is soluble in rectified spirit; but after a time reaction and decomposition occur.

Silver salts are decomposed when in contact with organic matter, especially in the presence of light or heat, the metal itself being liberated, or a black insoluble compound formed. Hence the value of the nitrate in the manufacture of indelible ink for marking linen; hence, too, the reason of the practice of rendering silver solutions clear by subsidence and decantation, rather than by filtration through paper; and hence the cause of those cases of actual combustion which have been known to occur in preparing pills containing oxide of silver and essential oil or other organic matter. Linen marked with such ink should not be cleansed by aid of bleaching-liquor, as the marked parts are then apt to be rapidly oxidized into perfectly rotten matter, holes resulting. Paul says the reaction is as follows: $Ag_2O + CaCl_2O_2 = 2AgCl + CaO + O_2$.

Oxide of Silver.

Fifth Synthetical Reaction.—To a few drops of solution of nitrate of silver add solution of potash or soda or lime-water; an olive-brown precipitate of oxide of silver (Ag_2O) occurs. The washed and dried oxide, like most silver compounds, is decomposed by heat, with production of metal. It is also readily reduced when triturated with oxidizable or combustible substances. (See the previous paragraph).

The *Argenti Oxidum*, U. S. P., may be thus made:

$$\underset{\text{Nitrate of silver.}}{2AgNO_3} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Oxide of silver.}}{Ag_2O} + \underset{\text{Nitrate of calcium.}}{Ca2NO_3} + \underset{\text{Water.}}{H_2O}$$

Methods of forming several other salts of silver are incidentally mentioned in the following analytical paragraphs.

(*b*) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—To a solution of a silver salt add hydrochloric acid or other soluble chloride; a white curdy precipitate of chloride of silver falls. Add nitric acid, and boil; the precipitate does not dissolve. Pour off the acid and add solution of ammonia; the precipitate dissolves. Neutralize the ammoniacal solution by an acid; the chloride of silver is reprecipitated.

This is the most characteristic test for silver. The precipitated chloride is also soluble in solutions of hyposulphite of sodium or cyanide of potassium—facts of considerable importance in photographic operations.

Other analytical reagents than the above are occasionally useful.——Sulphuretted hydrogen, or sulphydrate of ammonium, gives a black precipitate, sulphide of silver (Ag_2S), insoluble in alkalies.——Solutions of potash or soda give a brown precipitate, oxide of silver (Ag_2O), converted into a fulminating compound by prolonged contact with ammonia.——Phosphate of sodium gives a pale yellow precipitate, phosphate of silver (Ag_3PO_4), soluble in nitric acid and in ammonia.——Arseniate of ammonium gives a chocolate-colored precipitate, arseniate of silver (Ag_3AsO_4), already noticed in connection with arsenic acid.——Iodide or bromide of potassium gives a yellowish-white precipitate, iodide (*Argenti Iodidum*, U. S. P.) or bromide of silver (AgI or $AgBr$), insoluble in acids and only slightly soluble in ammonia.——Cyanide of potassium gives a white precipitate, cyanide of silver ($AgCy$), soluble in excess, sparingly soluble in ammonia, insoluble in dilute nitric acid, soluble in boiling concentrated nitric acid. *Argenti Cyanidum*, U. S. P., may be made by distilling a mixture of ferrocyanide of potassium and diluted sulphuric acid, and passing the resulting hydrocyanic acid into a solution of nitrate of silver: $HCy + AgNO_3 = AgCy + HNO_3$ (the precipitate is well washed and dried).——Yellow chromate of potassium (K_2CrO_4) gives a red precipitate, chromate of silver (Ag_2CrO_4).——Red chromate of potassium also gives a red precipitate, acid chromate of silver (Ag_2CrO_4,CrO_3).——Many organic acids afford insoluble salts of silver.——Several metals displace silver from solution, mercury forming in this way a crystalline compound known as the silver tree, or *Arbor Dianæ.*——In the blowpipe-flame, silver salts, placed on charcoal with a little carbonate of sodium, yield bright globules of metal accompanied by no incrustation as in the corresponding reaction with lead salts; the experiment may be performed with the nitrate, which first melts, and then, like all nitrates, deflagrates, yielding a white metallic coating of silver which slowly aggregates to a button.

Antidotes.—Solution of common salt, sal-ammoniac, or any other inert chloride should obviously be administered where large doses of nitrate of silver have been swallowed. A quantity of sea-water or brine would convert the silver into insoluble chloride, and at the same time produce vomiting.

QUESTIONS AND EXERCISES.

332. By what process is silver obtained from argentiferous galena?
333. What weight of English silver coin will yield one pound of pure nitrate of silver?
334. How may the metal be recovered from an impure mixture of silver salts?
335. Give a diagram showing the formation of nitrate of silver from the metal.
336. Describe the reaction of lime-water and nitrate of silver.
337. Mention the chief test for silver, and the precautions to be observed in order that silver salts may be distinguished from those of lead and mercury.
338. Name the antidote for silver.

DIRECTIONS FOR APPLYING SOME OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE OF THE METALS, COPPER, MERCURY (EITHER AS MERCUROUS OR MERCURIC SALT), LEAD, SILVER.

Add hydrochloric acid:—

Silver is indicated by a white curdy precipitate, soluble in ammonia.

Mercurous salts also by a white precipitate, turned black by ammonia.

Lead by a white precipitate, insoluble in ammonia. Confirm by boiling another portion of the hydrochloric precipitate in water: it dissolves.

If hydrochloric acid gives no precipitate, silver and mercurous salts are absent. Lead can only be present in very small quantity. Mercuric salts may be present. Copper may be present. Divide the liquid into three portions, and apply a direct test for each metal as follows:—

Lead is best detected by the sulphuric test; the tube being set aside for a time if the precipitate does not appear at once.

Mercury is best detected by the copper test. If present, here it occurs as mercuric salt.

Copper betrays itself by the blue color of the liquid under examination. Confirm by the ammonia test.

If the above reactions are not thoroughly conclusive, confirmatory evidence should be obtained by the application of some of the other reagents for copper, mercury, lead, or silver.

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALS, COPPER, MERCURY (EITHER MERCUROUS OR MERCURIC SALT, OR BOTH), LEAD, SILVER.

Add hydrochloric acid, filter, and wash the precipitate with a small quantity of cold water.

<table>
<tr><td colspan="3">Ppt.
Pb Hg(ous) Ag.
Wash with boiling water.</td><td rowspan="3">Filtrate.
Cu Hg(ic) Pb.
Divide into three portions.
Test for
Cu by AmHO; blue sol.
Hg (mercuric) by Cu; globules.
Pb by H_2SO_4; white ppt.*</td></tr>
<tr><td colspan="2">Ppt.
Hg(ous) Ag.
Add AmHO.</td><td rowspan="2">Filtrate.
Pb.
Add H_2SO_4, white ppt.*</td></tr>
<tr><td>Precipitate
Hg
(mercurous)
—black.</td><td>Filtrate.
Ag.
Add HNO_3
white ppt.</td></tr>
</table>

---

* Liquids containing only a small quantity of lead do not readily yield sulphate of lead on the addition of sulphuric acid. Before lead can be said to be absent, therefore, the liquid should be evaporated to dryness with one drop of sulphuric acid, and the residue digested in water; any sulphate of lead then remains as a heavy white insoluble powder.

SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF ORDINARY SALTS OF **ONE** OF THE ELEMENTS HITHERTO CONSIDERED.

Add hydrochloric acid.

<table>
<tr>
<td rowspan="3">Ppt.
Hg(ous) Pb Ag.
Add AmHO.
Hg(ous), black ppt.
Pb, ppt. still white.
Ag, ppt. dissolved.

Note I.—If HCl gave no precipitate, neither Hg(ous) nor Ag is present; and Pb only in minute amount, if at all.

Note II.—Hg obtained here must have existed in the solution as a mercurous salt.

Note III.—Sb is also precipitated by HCl, but is dissolved on adding more HCl; the Hg, Pb, and Ag precipitates are not soluble in excess of HCl.</td>
<td colspan="3">If HCl gave no precipitate, the metal is still in the liquid; pass H_2S through it.</td>
</tr>
<tr>
<td rowspan="2">Ppt.
Cu Hg(ic) Pb As Sb.
As, yellow ppt.
Sb, orange ppt.
Cu } Hg(ic) } Pb } black ppt.
Test original solution for Cu by AmHO; blue sol.
Hg by Cu; globules.
Pb by H_2SO_4; white ppt.

Note I.—If H_2S gave no precipitate, neither Cu, Hg, Pb, As, nor Sb is present.

Note II.—Hg and Pb may give colored precipitates (oxysulphides, etc.) with H_2S if too little of the latter has been passed through the solution.</td>
<td colspan="2">If H_2S gave no precipitate, the metal is still in the liquid; add AmCl, AmHO, and AmHS.</td>
</tr>
<tr>
<td>Ppt.
Fe Al Zn
Fe, black ppt.
Test original solution for ferric salt by K_4Fey (*dark* blue ppt.); and for ferrous salt by K_6Fdcy (*dark* blue ppt.).
Al } Zn } white ppt.
Test original solution by AmHO.
Al, white ppt. insoluble in excess.
Zn, white ppt. soluble in excess.</td>
<td>If AmHS, etc. gave no precipitate, the liquid may still contain either Ba, Ca, Mg, K, Na, or Am; add successively K_2CrO_4 for Ba, $Am_2C_2O_4$ for Ca, Na_2HPO_4 for Mg.
If neither Ba, Ca, nor Mg is found, examine the original solution for Am by KHO, Na by the flame-test, and K by $PtCl_4$.</td>
</tr>
</table>

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF ORDINARY SALTS OF **ANY OR ALL** OF THE ELEMENTS HITHERTO CONSIDERED.

(Read the "MEMORANDA" on the following page.)

Add hydrochloric acid, and filter.

<table>
<tr><td colspan="3">Precipitate
Hg(ous) Pb Ag.
Wash, boil with water, filter.</td><td colspan="10">Filtrate
Cu Hg(ic) Pb As Sb Fe Al Zn Ba Ca Mg K Na Am.
Pass H_2S through the liquid until it ceases to cause any alteration; filter.</td></tr>
<tr><td colspan="2">Precipitate
Hg(ous) Ag.
Add AmHO to the precipitate on the filter.</td><td rowspan="5">Filtrate
Pb.
Add H_2SO_4 white precipitate. (See footnote, p. 217.)</td><td colspan="3">Precipitate
Cu Hg(ic) Pb As Sb.
Wash, digest in AmHS, filter.</td><td colspan="7">Filtrate
Fe Al Zn Ba Ca Mg K Na Am.
Add AmHO, AmHS, and filter.</td></tr>
<tr><td rowspan="4">Precip.
Hg(ous).
Black precipitate.</td><td rowspan="4">Filtrate
Ag.
Add HNO_3: white precipitate.</td><td rowspan="4">Precipitate
Cu Hg(ic)
Wash, dissolve in a few drops of HNO_3 and HCl; evap. nearly to dryness; redissolve in H_2O, divide into three, and test for Cu by AmHO: blue solution. Hg by Cu; globules. Pb by H_2SO_4; white precip.</td><td colspan="2">Filtrate
As Sb.
Add $HC_2H_3O_2$ and boil; digest the precipitate in *strong* HCl; boil, dilute, filter.</td><td colspan="3">Precipitate
Fe Al Zn.
Wash, dissolve in HCl, boil (with a few drops of HNO_3 if necessary); add KHO, stir, filter.</td><td colspan="4">Filtrate
Ba Ca Mg K Na Am.
Add Am_2CO_3; boil, filter.</td></tr>
<tr><td rowspan="2">Precip.
As.
Yellow.</td><td rowspan="2">Filtrate
Sb.
Add H_2S. Orange precip.</td><td rowspan="3">Precipitate
Fe.
? Ferric or ferrous. Test original solution by yellow and red prussiate.</td><td colspan="2">Filtrate
Al Zn.
Neutralize by HCl; add AmHO, stir, filter.</td><td colspan="2">Precipitate
Ba Ca.
Wash, dissolve in $HC_2H_3O_2$, boil; and K_2CrO_4, filter.</td><td colspan="2">Filtrate
Mg K Na Am
Add Am_2HAsO_4; stir, filter.</td></tr>
<tr><td rowspan="2">Precip.
Al.
White precipitate.</td><td rowspan="2">Filtrate
Zn.
Add AmHS; white precip.</td><td rowspan="2">Precip.
Ba.
Yellow.</td><td rowspan="2">Filtrate
Ca.
Add $Am_2C_2O_4$: white precip.</td><td rowspan="2">Ppt.
Mg.
White.</td><td rowspan="2">Filtrate
K Na Am.
Evap., ignite, dissol. in H_2O; test for K by $PtCl_4$; yel. ppt. Na by flame; yellow. Am. in orig. sol. by NaHO.</td></tr>
<tr><td colspan="2">Confirm by testing original solution by the H tests.</td></tr>
</table>

OUTLINE OF THE PRECEDING TABLES.

HCl	H_2S		AmHS	Am_2CO_3	Am_2HAsO_4	
Hg. (as mercurous salt)	Cu	Insoluble in AmHS.	Zn	Ba	Mg	K
Pb (partially)	Hg (as mercuric salt)		Al	Ca		Na
	Pb (entirely)		Fe			Am
Ag	As	Soluble in AmHS.				
	Sb					

The practical student should examine solutions containing the common metals until he is able to analyze with facility and accuracy. In this way he will best perceive the peculiarities of each element and their general relations to each other. As the rarer metals are not included here, the tables are not complete analytical schemes; only general memoranda respecting them will therefore now be given.

MEMORANDA RELATING TO THE GENERAL ANALYTICAL TABLE (PAGE 219).

The *group-tests* adopted in the Table are, obviously, *hydrochloric acid*, *sulphuretted hydrogen*, *sulphydrate of ammonium*, *carbonate of ammonium*, and *arseniate of ammonium*. If a group-test produces no precipitate, it is self-evident that there can be no member of the group present. At first, therefore, add only a small quantity of a group-test, and if it produces no effect add no more; for it is not advisable to overload a solution with useless reagents; substances expected to come down as precipitates are not unfrequently held in the liquid by excess of acid, alkali, or strong aqueous solution of some group-reagent, thoughtlessly added. Indeed, experienced manipulators not unfrequently make preliminary trials with group-reagents on a few drops only of the liquid under examination; if a precipitate is produced, it is added to the bulk of the original liquid and the addition of the group-reagent continued; if a precipitate is not produced, the few drops are thrown away, and the unnecessary addition of a group-reagent thus avoided altogether, an advantage fully making up for the extra trouble of making a preliminary trial.——While shunning excess, however, care must be taken to avoid deficiency; a substance only partially removed from solution through the addition of an insufficient amount of a reagent will appear where not expected, be consequently mistaken for something else, and cause much trouble; this will not occur if the appearance, odor, or reaction of the liquid on test-paper be duly observed. It is also a good plan, when a group-reagent has produced a precipitate and the latter has been filtered out, to add a little more of the reagent to the clear filtrate; if more precipitate is produced, an insufficient amount of the group-test was introduced in the first instance; but the error is corrected by simply refiltering; if no precipitate occurs, the mind is satisfied and the way cleared for further operations.

Group-precipitates, or any precipitates still requiring examination, should, as a rule, be well washed before further testing; this is to remove the aqueous solution of other substances adhering to the precipitate (the mother-liquor, as it is termed), so that subsequent reaction may take place fairly between the reagent used and the precipitate only.——A precipitate is sometimes in so fine a state of division as to retard filtration by clogging the pores of the paper, or even to pass through the filter altogether; in these cases the mixture may be warmed or boiled (or a fresh quantity of the original solution may be warmed *before* the group-test is added), which usually causes aggregation of the particles of a precipitate, and hence facilitates the passage of liquids.

Division of Work.—It is immaterial whether a solution be first divided into group-precipitates or each precipitate be examined as soon as produced; if the former method be adopted, confusion will be avoided by labelling or marking the funnels or papers holding the precipitate, "the HCl ppt.," "the H_2S ppt.," and so on.

The colors and general appearance of the various sulphides and hydrates precipitated should be borne in mind, as the absence of other bodies, as well as the presence of those thrown down, is often at once thus indicated.

Application of confirmatory tests must be frequent.

Results of analysis should be recorded neatly in a memorandum-book.

The various reactions which occur in an analysis have already come before the reader in going through the tests for the individual metals or in other analytical operations; it is unnecessary, therefore, again to draw out equations or diagrams. But the reactions should be thought over, and if not perfectly clear to the mind, be written out again and again till thoroughly understood.

QUESTIONS AND EXERCISES.

339. Give processes for the qualitative analysis of liquids containing the following substances:—

a. Antimony and Mercurous salt.
b. Lead and Calcium.
c. Silver and Mercurous salt.
d. Lead and Mercuric salt.
e. Copper and arsenicum.
f. Arsenicum and Antimony.
g. Aluminium and Zinc.
h. Iron and Copper.
i. Magnesium, Calcium, and Potassium.
j. Silver, Antimony, Zinc, Barium, and Ammonium.

340. Enumerate the so-called group-tests.

341. Give a general sketch of the method of analyzing a solution suspected to contain two or more salts of common metals.

342. Classify the common metals according to their analytical relations.

METALS OF MINOR PHARMACEUTICAL IMPORTANCE.

Thus far has been considered, somewhat in detail, the chemistry of the common metals, salts of which are frequently used in medicine or in testing medical substances. These are—

Potassium, Sodium, Ammonium (?),
Barium, Calcium, Magnesium,
Zinc, Aluminium, Iron.
Arsenicum, Antimony, Copper,
Mercury, Lead, Silver.

Of the remaining metals, nine have considerable interest for the student of medicine or of pharmacy, namely:—

Lithium, Cerium,
Manganese, Chromium,
Tin, Gold,
Platinum, Cadmium,
Bismuth.

Compounds of three more occasionally come under notice—

Strontium, Cobalt, Nickel.

These twelve metals of minor pharmaceutical interest may be shortly studied, a few only of the reactions of each (just those mentioned in the following pages) being performed. When all have been thus treated, their respective positions in the analytical groups will be indicated, and a tabular scheme by which an analysis of a solution containing any metal may be effected. Thus, step by step, we may learn how to analyze almost any substance that may occur, and know to what extent the presence of a rarer will interfere with the ordinary tests for a common element; additional illustrations of the working of chemical laws will be acquired, and the store of chemical and pharmaceutical facts increased. The opportunity thus afforded for improvement in habits of neatness in manipulation, precision, and classification furnishes another and no mean reason why such experiments should be prosecuted, the direct value of which may not be considerable to medical and pharmaceutical learners.

LITHIUM.

Symbol L. Atomic weight 7.

Lithium is widely distributed in nature, but usually in minute proportions compared with other elements. A trace of it may be found in most soils and waters, a Cornish spring containing considerable quantities as chloride.

One salt used in medicine is the *Citrate* ($L_3C_6H_5O_7$) (*Lithii Citras*, U. S. P.), occurring in white deliquescent crystals or powder, prepared by dissolving 50 grains of the *Carbonate* (L_2CO_3) and 95 of citric acid (50 to 95 if both are quite pure) in 1 ounce of water, evaporating to a low bulk, and setting aside in a dry place to crystallize, or at once evaporating to dryness and powdering the residue. The crystals have the formula $L_3C_6H_5O_7,4H_2O$; dried at 212° F., $L_3C_6H_5O_7,H_2O$ (Umney).

$$\underset{\substack{\text{Carbonate}\\\text{of lithium.}}}{3L_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\substack{\text{Citrate of}\\\text{lithium.}}}{2L_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

The benzoate (*Lithii Benzoas*, , $LC_7H_5O_2$, U. S. P.), bromide (*Lithii Bromidum*, LBr, U. S. P.), and salicylate (*Lithii Salicylas*, $2LC_7H_5O_3,H_2O$, U. S. P.) may be similarly prepared from the respective acids.

The above-named lithium salts are officially tested as follows, the Bromide being acted upon directly without ignition :—

"On dissolving the residue, left on ignition [of either salt] in diluted hydrochloric acid, and evaporating the filtered solution to dryness, 1 part of the residue should be completely soluble in 3 parts of absolute alcohol, which, when ignited, should burn with a crimson flame, and the addition of an equal volume of stronger ether to the alcoholic solution should produce no precipitate (salts of alkalies). On dissolving another portion of the residue in a small quantity of water, the solution should produce no precipitate with test-solution of oxalate of ammonium (salts of alkaline earths). The aqueous solution should remain unaffected by hydrosulphuric acid or sulphide of ammonium (abs. of metals)."—U. S. P.

The carbonate (*Lithii Carbonas*, U. S. P.) is a white granular powder obtained from the minerals which contain lithium; namely, lepidolite (from λεπὶς, *lepis*, a scale, and λίθος, *lithos*, a stone; it has a scaly appearance), triphane (from τρεῖς, *treis*, three, and φαίνω, *phainō*, I shine), or spodumene (from σποδόω, *spodŏō*, I reduce to ashes, in allusion to its exfoliation in the blowpipe-flame), and petalite (from πέταλον, *petalon*, a leaf; its character is leafy and laminated). Each contains silicate of aluminium, with fluoride of potassium and lithium in the case of lepidolite, and silicate of sodium and lithium in the others. *Liquor Lithiæ Effervescens*,

B. P., is a solution of 10 grains of carbonate of lithium in 1 pint of water charged with 7 times its volume of carbonic acid gas and kept in ordinary aërated-water bottles. "Half a pint, evaporated to dryness, yields 5 grains of a white solid residue, answering to the tests for carbonate of lithium. . . . Ten grains of the latter salt neutralized with sulphuric acid, and afterwards heated to redness, leave 14.86 grains of dry sulphate of lithium, which, when redissolved in distilled water, yields no precipitate with oxalate of ammonium or solution of lime," indicating absence of salts of calcium and aluminium. Citrate of lithium should yield by incineration 52.8 per cent. of white carbonate of lithium.

*Urate of lithium** is more soluble than urate of sodium; hence lithium preparations are administered to gouty patients in the hope that urate of sodium, with which such systems are loaded, may be converted into urate of lithium and removed.

In chemical position lithium stands between the alkaline and the alkaline-earth metals, its hydrate, carbonate, and phosphate being slightly soluble in water. The double chloride of platinum and lithium also is soluble in water. Its atom is univalent, L′.

Analytical Reaction.—Moisten the end of a platinum wire with solution of a minute particle of solid lithium salt, and introduce it into the flame of a Bunsen burner or other slightly colored flame (spirit-lamp or blowpipe-flame); a magnificent crimson tinge is imparted.

The light thus emitted by ignited lithium vapor is of a purer scarlet than that given by strontium, the next element. When the flames are examined by spectral analysis (physically analyzed by a prism), the red rays are, in the case of strontium, found to be associated with blue and yellow, neither of which is present in the lithium light, blue lithium rays only appearing at temperatures much higher than those of ordinary air-gas flames.

STRONTIUM.

Symbol Sr. Atomic weight 87.4.

Source.—Strontium is not widely distributed in nature, but the carbonate ($SrCO_3$) known as *strontianite*, and the sulphate ($SrSO_4$), known as *celestine* (from *cœlum*, the sky, in allusion to its occasional bluish color), are by no means rare minerals.

Salts of strontium are not employed in medicine. They are chiefly used by firework-manufacturers in preparing red fire. The color they impart to flame is a beautiful crimson—ignited strontium vapor emitting red rays, as already explained. Nitrate of strontium ($Sr2NO_3$) is best for pyrotechnic compositions, its oxygen enabling it to burn freely when mixed with charcoal, sulphur, etc. It, or any salts, may be obtained by dissolving the carbonate in the appropriate acid, or by igniting the cheaper sulphate with coal, whereby sulphide (SrS) is produced, and dissolving this in acid.

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* Urates will be considered subsequently in connection with uric acid.

The position of strontium among the chemical elements is between barium and calcium; its sulphate is very sparingly soluble in water. Its atom, like those of barium and calcium, is bivalent (Sr″).

Analytical Reactions (Tests).

First Analytical Reaction.—To a solution of a strontium salt ($Sr2NO_3$ or $SrCl_2$) add carbonate of ammonium; a white precipitate of carbonate of strontium ($SrCO_3$) falls.

Second Analytical Reaction.—To a solution of a strontium salt add sulphuric acid previously so diluted that it will not precipitate calcium salts, or add an equally dilute solution of any sulphate (*e. g.*, that of calcium itself); a white precipitate of sulphate of strontium ($SrSO_4$) falls. The formation of this precipitate is promoted by stirring and setting the liquid aside for some time.

Barium is precipitated immediately under similar circumstances.

Third Analytical Reaction.—To a dilute solution of a strontium salt add yellow chromate of potassium; no precipitate falls.

Barium may be separated from strontium by chromate of potassium, that reagent at once precipitating barium from aqueous or acetic solutions. The value of the reaction is enhanced if the solutions be dilute and if acetic acid or acetate of ammonium be present, chromate of strontium being far more soluble in such fluids than in water (Ransom). It is also more soluble in cold than in hot fluids.

Fourth Analytical Reaction.—Insert a fragment of a strontium salt in the blowpipe-flame, or other equally colorless flame, or hold the end of a platinum wire dipped into a strontium solution in the flame; a crimson color is imparted.

Other Analytical Reactions.—Alkali-metal phosphates, arseniates, and oxalates give white insoluble precipitates with strontium as with barium and calcium.——Strontium, like calcium, but unlike barium, is not precipitated by hydrofluosilicic acid.

Cerium. Ce. At. wt. 22.—This element occurs in the mineral cerite (a silicate of iron, calcium, and the three rare metals, cerium, lanthanum, and didymium); also occasionally as impure fluoride, carbonate, and phosphate. The oxalate of cerium, a white granular powder, is the only official salt; it may be obtained from cerite by boiling the powdered mineral in strong hydrochloric acid for several hours, evaporating, diluting, and filtering to separate silica; adding ammonia to precipitate hydrates of all the metals except calcium;

filtering off, washing, redissolving in hydrochloric acid, and adding oxalic acid to precipitate oxalate of cerium. The preparation will still contain oxalates of lanthanum and didymium; it is therefore strongly calcined, the resulting oxides of lanthanum and didymium dissolved out to some extent by boiling with a concentrated solution of chloride of ammonium, the residual oxide of cerium dissolved in boiling hydrochloric acid, and oxalate of ammonium added to precipitate white, granular oxalate of cerium ($Ce_2{}'''3C_2O_4,9H_2O$). According to Hartley the precipitated hydrates are treated with chlorine, by which ceric hydrate is left insoluble and the other hydrates converted into soluble hypochlorites.

Oxalate of cerium (*Cerii Oxalas*, U. S. P.) is decomposed at a dull red heat, 48 per cent. of a yellow, or, more generally, a salmon-colored, mixture of oxides remaining; usually the didymium present gives the ignited residue a reddish or reddish-brown color; it is then soluble in boiling hydrochloric acid (without effervescence; indicating, indirectly, absence of earthy and other carbonates or oxalates), and the solution gives, with excess of a saturated solution of sulphate of potassium, a crystalline precipitate of double sulphate of cerium and potassium. Alumina mixed with oxalate of cerium may be detected by boiling with solution of potash, filtering, and adding excess of solution of chloride of ammonium, when a white flocculent precipitate of hydrate of aluminium will be obtained. Oxide of zinc is revealed on boiling in potash and adding sulphide of ammonium, when white sulphide of zinc falls. The oxalic radical is recognized by neutralizing the potash solution by acetic acid and adding chloride of calcium; white oxalate of calcium is then precipitated; this precipitate, though insoluble in acetic, should be wholly dissolved by hydrochloric acid. Acid or neutral cerium solutions give with acetate of sodium and peroxide of hydrogen a brownish-red color (Hartley).

According to H. G. Greenish, most samples of oxalate of cerium have as impurities traces of lead, iron, and magnesium.

MANGANESE.

Symbol Mn. Atomic weight 54.

Source.—Manganese is a constituent of many minerals, and as black oxide, or dioxide, or binoxide (MnO_2) (*Mangani Oxidum Nigrum*, U. S. P., "containing not less than 66 per cent. of pure oxide, MnO_2"), or *pyrolusite* (from πῦρ, *pur*, fire, and λύσις, *lusis*, a loosing or resolving, in allusion to the readiness with which it is split up by heat into a lower oxide and oxygen), occurs frequently in abundance in the south-west of England, Aberdeenshire, and most of the countries of Europe. It is met with as a steel-gray mass of prismatic crystals or in black shapeless lumps.

The chemical position of manganese is close to iron and three other metals still to be considered—cobalt, nickel, and chromium. Its atom apparently has sexivalent affinities, as seen in manganate of potassium, (K_2MnO_4); but commonly it is quadrivalent (Mn^{IV}) or bivalent (Mn'').

Uses.—Metallic manganese is only used in alloy with iron in the manufacture of some varieties of steel. The black oxide is an important agent in the production of chlorine, the preparation of green and red disinfecting manganates, purple glass, and black glazes for earthenware.

Reactions having both Synthetical and Analytical Interest.

First Reaction.—Boil a few grains of black oxide of manganese with some drops of hydrochloric acid until chlorine ceases to be evolved; add water, and filter; the filtrate is a solution of manganous chloride ($MnCl_2$).

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

This is the reaction commonly applied in the preparation of chlorine gas. It is also a ready method of preparing a manganous salt for analytical experiments. Coupled with the application of reagents to the filtrate, the reaction is that by which a black powder or mineral would be recognized as black oxide of manganese. Black oxide of manganese dissolves in cold hydrochloric acid, forming a dark-brown solution of a higher chloride or chlorides, $MnCl_3$, Mn_2Cl_7, or, possibly, $MnCl_4$.

Second Reaction.—Heat a particle of a manganese compound with a grain or two of carbonate and hydrate of potassium and a fragment of nitrate or chlorate of potassium on platinum foil in the blowpipe-flame; a green mass containing *manganate of potassium* (K_2MnO_4) results. Boil the foil in a little water; the green manganate dissolves and soon changes to solution of the purple *permanganate of potassium* ($K_2Mn_2O_8$).

This is a delicate analytical test for manganese.

The reaction is similar to that by which permanganate of potassium (*Potassii Permanganas*, U. S. P.) is prepared for use in volumetric analysis. Equations showing the exact action which occurs in making the salt according to the process of the British Pharmacopœia have already been given in connection with the compounds of potassium (*vide* p. 76). The proportions of ingredients and details of the operation are as follows:—

Reduce 3½ parts (for experiment each "part" may be ⅛th oz.) of chlorate of potassium to fine powder, and mix it with 4 of black oxide of manganese; put the mixture into a porcelain basin, and add to it 5 parts of solid caustic potash, previously dissolved in 4 parts of water. Evaporate to dryness, stirring diligently to prevent spirting. Pulverize the mass, put it into a covered Hessian or Cornish crucible, and expose it to a dull red heat (not higher) for an hour (20 or 30 minutes for quantities of 1 or 2 oz.), or till it has assumed the condition of a semi-fused mass. Allow to cool, pulverize, and boil with about 30 parts of water. Let the insoluble matter subside, decant the fluid, boil again with about 10 parts of water, again decant, neutralize the united liquors accurately with diluted sulphuric acid (or, better, carbonic acid gas), and evaporate till a pellicle forms. Set aside to cool and crystallize. Drain the crystalline mass, boil it in 6 parts of water, and strain through a funnel the throat of which is slightly obstructed by a little asbestos or gun-cotton. Let the fluid cool and crystallize, drain the dark purple slender prismatic crystals, and dry them by placing under a bell-jar over a vessel containing sulphuric acid.

Instead of converting the manganate into permanganate by ebullition, by which one-third of the manganate is lost, Städeler recommends chlorine to be passed through the cold solution until the green color is entirely changed to purple.

Solutions of the manganates of potassium and sodium are in common use as disinfectants under the name of Condy's Fluid. They act by oxidizing organic matter, the manganic or permanganic radical being reduced to black manganic oxide, or even a lower oxide. The reason for using asbestos instead of paper in filtering the solutions will now be understood.

The changes in color which the green mass of the above process undergoes when dropped into warm water procured for it the old name of *mineral chameleon.*

Third Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in the blowpipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of a manganese compound, or touch it with a drop of solution. Again fuse the borax, using the point of the flame; a bead of a violet or amethystine tint is produced.

This is a good analytical reaction. It has also synthetical interest, illustrating the use of black oxide of manganese in producing common purple-tinted glass.

Expose the bead to the reducing part of the flame, the part nearer to the blowpipe, where there are highly heated hydrocarbon gases greedy of oxygen; the color disappears.

This is owing to the reduction of the manganic compound to a manganous condition, in which it no longer possesses peculiar coloring-power. This action also illustrates the use of black oxide of manganese in glass-manufacture. Glass when first made is usually of a green tint, owing to the presence of ferrous impurities; the addition of manganic oxide to the materials converts the ferrous into ferric compounds, which have comparatively little colorific power, it itself being thereby reduced to manganous oxide, which also gives but little color. If excess of manganic oxide be added, a purple tint is produced.

Reactions having Analytical Interest (Tests).

Fourth Reaction.—Through a solution of a manganous salt acidified by hydrochloric acid pass sulphuretted hydrogen; no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of a yellowish-pink or flesh-tinted precipitate of manganous sulphide (MnS) in a hydrous state.

This reaction is characteristic, sulphide of manganese being the only flesh-colored sulphide known. The salt used may be the manganous chloride obtained in the first reaction; but such crude solutions usually give a black precipitate with sulphydrate of ammonium, owing to the presence of iron. The latter element may be precipitated, however, on adding excess of ammonia (and rapidly filtering; oxygen will be absorbed and most of the manganese also precipitated) or on boiling the manganous solution with a very little carbonate of sodium, which attacks the ferric salt in preference to the manganous. *Pure* manganous chloride may be similarly obtained on boiling the impure solution with manganous carbonate; the latter decomposes the ferric chloride with production of ferric hydrate and more manganous chloride, and evolution of carbonic acid gas.

To the recently precipitated manganous sulphide add acetic acid; it is dissolved.

This solubility enables manganese to be separated from nickel, cobalt, and zinc, whose sulphides are insoluble in weak acetic acid. To express the fact in another way—manganese is not precipitated by sulphuretted hydrogen from a solution containing free acetic acid only.

Fifth Reaction.—To solution of manganous salt add ammonia; a white precipitate of manganous hydrate (Mn2HO) falls. Add excess of ammonia; some of the precipitate is dissolved, and may be detected in the quickly filtered solution by sulphydrate of ammonium. But both precipitate and solution rapidly absorb oxygen, the manganese passing into a more highly oxidized condition in which it is insoluble in ammonia.

The fixed alkalies give a similar precipitate *insoluble* in excess. The precipitate rapidly absorbs oxygen, becomes brown, and gradually passes into a higher oxide.

Sixth Reaction.—Heat a little black oxide of manganese in a test-tube with sulphuric acid; oxygen is evolved and sulphate of manganese formed (*Mangani Sulphas*, $MnSO_4,4H_2O$, U. S. P.); add water, boil, filter, evaporate, and set aside to crystallize. Larger quantities are made in a similar manner.

Sulphate of manganese ($MnSO_4,5H_2O$) occurs in colorless or pale rose-colored, transparent crystals, which, when deposited from a solution at a temperature between 68° and 86°, have the form of right rhombic prisms, and contain four molecules of water (U. S. P.). This salt is very soluble in water. Other sulphates containing 1, 2, 3, and 9 of water are known. The solution is not colored by tincture of nutgall (a black shows iron), but affords with caustic alkalies a white precipitate (Mn2HO), which, by exposure to the air, soon absorbs oxygen, and becomes brown. Sulphydrate of ammonium throws down a flesh-colored precipitate (MnS), and ferrocyanide of potassium a white one (Mn_2Fcy).

Many other reactions occur between manganese salts and various reagents, but are of no particular synthetical or analytical interest.

A good method proposed by Crum, for detecting minute quantities of manganese, consists in adding dilute nitric acid and either red lead or the puce-colored oxide or peroxide of lead to the solution, and then boiling; a red tint, said to be due to permanganic acid, is imparted to the liquid.

COBALT.

Symbol Co. Atomic weight 58.9.

Source.—Cobalt occurs sparingly in nature as the arsenide ($CoAs_2$), or *tin-white cobalt*, and occasionally as a double arsenide and sulphide ($CoAs_2,CoS_2$), or *cobalt glance* (from *glanz*, brightness, in allusion to its lustre).

Uses.—Its chief use is in the manufacture of blue glass, the color of which is due to a compound of cobalt. Cobalt is also the coloring constituent of *smalt* (from *smelt*, a corruption of *melt*), a finely-ground sort of glass, used as a blue pigment by paper-stainers and others, and employed also by laundresses to neutralize the yellowish appearance of washed linen.

The salts of cobalt may be obtained from the oxide (CoO), and the oxide from *zaffre*, a mixture of sand and roasted ore.

Quantivalence.—The atom of cobalt often exhibits quadrivalent affinities, but still more often exerts only bivalent powers (Co''). Cobalt has analytical relations with zinc, nickel, and manganese, and may be regarded as a member of the iron group.

Analytical Reactions (*Tests*).

First Analytical Reaction.—Pass sulphuretted hydrogen through a solution of a salt of cobalt—the chloride ($CoCl_2$) or nitrate ($Co2NO_3$), for example; no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of black sulphide of cobalt (CoS).

The moist precipitate slowly absorbs oxygen from the air, becoming converted into sulphate of cobalt ($CoSO_4$).

Second Analytical Reaction.—Add ammonia gradually to a cobalt solution; a blue precipitate of impure hydrate of cobalt (Co2HO) falls. Add excess of ammonia; the precipitate is dissolved, yielding a liquid somewhat more reddish-brown than the original solution.

A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in a blowpipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of a cobalt compound, or touch it with a drop of solution. Again fuse the borax; a blue bead results.

This is a delicate test for cobalt. From what has previously been said, it will be seen that this experiment has also considerable synthetical interest.

Fourth Analytical Reaction.—To a solution of a salt of cobalt add two or three drops of hydrochloric acid, then excess of solution of cyanide of potassium, and boil for ten minutes; oxygen is absorbed, and cobalticyanide of potassium ($K_6Co_2Cy_{12}$) formed. Add hydrochloric acid, and boil the mixture (in a fume-cupboard, to avoid inhalation of any hydrocyanic acid); the excess of cyanide of potassium is thus decomposed, but the cobalticyanide is unaffected. Now add excess of solution of potash; the cobalticyanide of potassium is decomposed, but the cobalt remains dissolved in the alkaline liquid.

Nickel under similar circumstances is precipitated, the reaction thus affording means of separating these closely allied metals from each other.

Other Reactions between a cobalt solution and different reagents may be performed, and various precipitates obtained; but these have no special analytical interest.

Invisible Ink.—Many salts of cobalt containing water of crystallization are light red, the anhydrous more or less blue. Prove this by writing some words on paper with a solution of chloride of cobalt sufficiently dilute for the characters to be invisible when dry; hold the sheet before a fire or over a flame; the letters at once become visible, distinct, and of a blue color. Breathe on the words, or set the sheet aside for a while; the characters are once more invisible, owing to absorption of moisture. Hence solution of chloride of cobalt forms one of the so-called *sympathetic inks.*

NICKEL.

Symbol Ni. Atomic weight 58.

Nickel is, chemically, closely allied to cobalt, the ores of the two metals being commonly associated in nature. Indeed, it is from *speiss*, an arsenio-sulphide of nickel obtained in the manufacture of smalt, a pigment of cobalt already mentioned, that most of the nickel met with in commerce is obtained. It is much used in the preparation of the white alloy known as German or nickel silver.

Quantivalence.—Nickel exerts bivalent activity (Ni'') in its ordinary compounds. Its salts and their solutions are usually green. They are chiefly made, directly or indirectly, from the metal itself.

Analytical Reactions (Tests).

First Analytical Reaction.—Pass sulphuretted hydrogen through a solution of a salt of nickel—chloride ($NiCl_2$), nitrate ($Ni2NO_3$), or sulphate ($NiSO_4$); no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of black sulphide of nickel (NiS).

Note.—When sulphate of nickel is precipitated by the direct addition of the common yellow solution of sulphydrate of ammonium, which always contains free sulphur, there is much difficulty in filtering the mixture, owing to the slight solubility of sulphide of nickel in the reagent and the formation of some sulphate of nickel ($NiSO_4$), oxygen being absorbed from the air by the sulphide. This may be avoided by warming the mixture and using freshly-made sulphydrate of ammonium, in which the sulphide of nickel is insoluble; or, where practicable, the salt of nickel may be precipitated from an ammoniacal solution by sulphuretted hydrogen.

Second Analytical Reaction.—Add ammonia drop by drop to a nickel solution; a pale-green precipitate of hydrate of nickel ($Ni2HO$) falls, especially on boiling the mixture. Add excess of ammonia; the precipitate dissolves, yielding a bluish rather than the original green-colored solution.

A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Reaction.—Nickel salts color a borax bead, when hot, a reddish-yellow tint; the reaction is not very serviceable analytically.

Fourth Analytical Reaction.—To a solution of a salt of nickel add solution of cyanide of potassium; cyanide of nickel ($NiCy_2$) is precipitated. Add excess of solution of cyanide of potassium; the precipitate is dissolved with formation of double cyanide of nickel and potassium ($NiCy_2,2KCy$). Next add hydrochloric acid, and boil the mixture (in a fume-cupboard), adding a little hydrochloric acid from time to time until all smell of hydrocyanic acid has disappeared. Lastly, add *excess* of solution of potash; hydrate of nickel is precipitated.

Qualitative Separation of Cobalt and Nickel.

The foregoing reaction serves for the separation of nickel from cobalt. On adding excess of hydrochloric acid to a solution containing the two metals, together with cyanide of potassium, a precipitate of cyanide of nickel and cobalticyanide of nickel occurs. By ebullition with excess of hydrochloric acid the cyanide of nickel is decomposed, chloride of nickel going into solution. On then adding excess of potash, hydrate of nickel is precipitated. The cobalticyanide of nickel is not decomposed by the acid; but is by the alkali, its cobalt going into solution and its nickel remaining insoluble as hydrate.

After filtering off the nickel, cobalt is detected in the filtrate by evaporating to dryness and testing the residue with borax in the blowpipe-flame.

W. R. Dunstan thus modifies this process:—

To the acidified solution containing the two metals potassium cyanide is added in excess until a clear solution is obtained. To a portion of this liquid a few drops of yellow ammonium sulphide are added; a dark-red coloration indicates cobalt. This reaction is very characteristic, and is not interfered with by the presence of nickel. The solution does not give the reaction after exposure to the air or after ebullition. The remainder of the solution is boiled for a few minutes, and when cool hydrochloric acid added in excess; if both metals are present a dense bluish-white precipitate occurs. The solution is boiled for some time till free from hydrocyanic acid, the precipitate remaining insoluble, which is a sure indication of the presence of both metals. To this liquid containing the precipitate large excess of potassium hydrate is added. The precipitate of nickelous cobalticyanide disappears, and is replaced by a pale-green flocculent precipitate of nickelous hydrate.

The reducing action of glycerin on nickelic hydrate ($Ni_2 6HO$), and the absence of any similar action on cobaltic hydrate affords another method of separating the metals. (See *Pharmaceutical Journal*, May 31, 1879.)

Another Process.—To any solution containing cobalt and nickel add excess of ammonia, and then enough solution of ferridcyanide of potassium to dissolve any precipitate. If cobalt be present a reddish-brown color is produced in the liquid, due to the formation and solution of ferridcyanide of cobalt. Now add solution of ferrocyanide of potassium; a whitish precipitate of ferrocyanide of nickel appears, either at once, or, if the liquid is very weak, on *partially* neutralizing the free ammonia by hydrochloric acid. The ammonia must not be entirely neutralized by acid, nor enough acid added to decompose the reddish ferridcyanide of cobalt. If these precautions be not observed, a greenish-white precipitate of ferrocyanide of cobalt may be formed, and be mistaken for the ferrocyanide of nickel.

The value of this method (Skey and Davies) turns on the facts that ferridcyanide of nickel is not a colored body, while ferridcyanide of cobalt is reddish-brown, and that ferridcyanogen has apparently, *in ammoniacal solution*, greater affinity for cobalt than for nickel, while ferrocyanogen has, apparently, greater affinity for nickel than for cobalt. The formulæ of these so-called ferrocyanides and ferridcyanides of cobalt and nickel have not been definitely ascertained.

Other reactions between a nickel solution and various reagents give, in many cases, insoluble precipitates which, from their green color, are occasionally useful in distinguishing nickel from allied elements.

CHROMIUM.

Symbol Cr. Atomic weight 52.4.

Source.—The chief ore of chromium is chrome ironstone, a mixture of the oxides of the metals (FeO,Cr_2O_3), occurring chiefly in the United States and Sweden. In constitution it seems to resemble magnetic iron ore (FeO,Fe_2O_3).

Preparation of Red Chromate of Potassium.—On roasting the powdered ore with carbonate of potassium and nitre, yellow chromate of potassium (K_2CrO_4) is obtained; the mass, treated with acid, yields red or bichromate (K_2CrO_4,CrO_3) (*Potassii Bichromas.* U. S. P.); from this salt other chromates are prepared, and by reduction, as presently explained, the salts of chromium itself. The yellow and orange chromates of lead are largely used as pigments.

Note on Constitution.—Red chromate of potassium is a somewhat abnormal salt, containing, probably, neutral chromate associated with chromic anhydride. The value of chromates as chemical reagents is alluded to in connection with chromate of barium (p. 102). Heated strongly in a crucible, red chromate of potassium splits up into yellow chromate, glistening oxide of chromium, and oxygen.

Quantivalence.—Chromium stands in close chemical relation to iron, aluminium, and manganese. Its atom is sexivalent if the formula of the fluoride (CrF_6) be correct. Like iron and aluminium, it is trivalent, as seen in chromic chloride (Cr_2Cl_6), but sometimes exerts only bivalent activity, as in chromous chloride ($CrCl_2$).

Passage of Chromium from the Acidulous to the Basylous Side of Salts.—Through an acidified solution of red chromate of potassium pass sulphuretted hydrogen; sulphur is deposited, and a green salt of chromium remains in solution. chloride (Cr_2Cl_6) if hydrochloric acid be used, and sulphate (Cr_23SO_4) if sulphuric be the acid employed. Boil the liquid to expel excess of sulphuretted hydrogen, filter, and reserve the solution for subsequent experiments. (For an equation of this reaction, see p. 235.)

Alcohol, sugar, or almost any substance which is tolerably liable to oxidation, will answer as well as sulphuretted hydrogen.

Sulphate of chromium ($Cr_2 3SO_4$), like sulphate of aluminium ($Al_2 3SO_4$), unites with alkali-metal sulphates to form *alums*, which resemble common alum both in crystalline form, and, as far as we know, in internal structure: they are of purple color.

REACTIONS.

Chromium as *Chromic Acid*, or other *Chromate*.—This is the state in which chromium will usually be met with, the most common salt being the red chromate or bichromate of potassium. Mix four volumes of a cold, saturated aqueous solution of red chromate of potassium with five of oil of vitrol; on cooling, *chromic anhydride* (CrO_3), *Acidum Chromicum*, U. S. P., separates in crimson needles. After well draining, the crystals may be freed from adhering sulphuric acid by washing once or twice with nitric acid: the latter may be removed by passing dried and slightly warmed air through a tube containing the crystals. In contact with moisture chromic anhydride takes up water and forms solution of true chromic acid (H_2CrO_4). Chromic anhydride is a powerfully corrosive oxidizing agent. It melts between 356° and 374° F.

The oxygen in chromic acid and other chromates, and in manganates, permanganates, black oxide of manganese, and puce-colored oxide of lead, is in a physically different state from that in peroxide of hydrogen, peroxide of barium, and similar compounds. On bringing chromic acid or the above acidified solution of red chromate of potassium into contact with solution of peroxide of hydrogen, a strong effervescence of oxygen ensues. According to Schönbein and Brodie the oxygen of chromic acid is in the negative or ozonic state, while that of peroxide of hydrogen is in the positive or so-called antozonic condition. Both are equally active, but neutralize each other, forming neutral or ordinary oxygen.

In the analytical examination of solutions containing chromates, the chromium will always come out in the state of green chromic hydrate along with ferric hydrate and alumina, the prior treatment by sulphuretted hydrogen reducing the chromium in the molecule to the lower state, thus:—

$$K_2CrO_4,CrO_3 + 8HCl + 3H_2S = Cr_2Cl_6 + 2KCl + 7H_2O + S_3.$$

Chromium having been found in a solution, its condition as chromate may be ascertained by applying to the original solution salts of barium, mercury, lead, and silver. (See the various paragraphs relating to those metals.)

$Ba2NO_3$ gives yellow $BaCrO_4$ with chromates.
Hg_22NO_3 " red Hg_2CrO_4 "
$AgNO_3$ " " Ag_2CrO_4 "
" " " Ag_2CrO_4,CrO_3 with bichromates.
$Pb2C_2H_3O_2$ " yellow $PbCrO_4$ with both.

Nitrate of barium does not completely precipitate bichromates, bichromate of barium being soluble in water; the chromate of barium is insoluble in water or acetic acid, but soluble in hydrochloric or nitric acid. Mercurous nitrate does not wholly precipitate bichromates: mercuric nitrate or chloride only partially precipitates chromates, and does not precipitate bichromates. The mercurous chromate is insoluble, or nearly so, in diluted nitric acid. The silver chromates are soluble in acids and alkalies. Acetate of lead precipitates chromates and bichromates, acetic acid being set free in the latter case.

A delicate reaction for dry chromates will be found in the formation of *chlorochromic anhydride* (CrO_2Cl_2). A small portion of the chromate is placed in a test-tube with a fragment of dry chloride of sodium and a drop or two of oil of vitrol, and the mixture heated; red irritating fumes of chlorochromic *anhydride* are evolved, and condense in dark-red drops on the side of the tube.

Large quantities of pure distilled chlorochromic anhydride are obtained by the same reaction, the operation being conducted in a retort, with thoroughly dry materials, for the compound is decomposed by water. It may be regarded as chromic anhydride in which an atom of oxygen is displaced by an equivalent quantity (two atoms) of chlorine. It is not used in medicine, but is of interest to the chemical student as being an illustration of a large class of similar bodies—*chloro-acidulous* or *chloro-anhydrous compounds*. The reaction is also occasionally serviceable for the detection of chlorides.

Analytical Reactions of Chromium Salts (*Tests*).

First Analytical Reaction.—To solution of a salt of chromium (chloride, sulphate, or chrome alum) add sulphydrate of ammonium; a bulky green precipitate of chromic hydrate (Cr_26HO), containing a large quantity of water (7 molecules, $7H_2O$), is precipitated.

$$Cr_2Cl_6 + 6AmHS + 6H_2O = Cr_26HO + 6AmCl + 6H_2S.$$

Second Analytical Reaction.—To solution of a chromium salt add ammonia; chromic hydrate is precipitated, insoluble in excess.

Third Analytical Reaction.—To solution of a chromium salt add solution of potash or soda, drop by drop; chromic hydrate is precipitated. Add excess of the fixed alkali; the precipitate is dissolved. Boil well the solution; the chromic hydrate is reprecipitated.

Iron, Chromium, and Aluminium Salts, chemically so alike, may be separated by this reaction. Ferric hydrate is insoluble in solutions of the fixed alkalies, cold or hot; chromium hydrate, soluble in cold but not in hot; hydrate of aluminium, in both. To a solution containing all three metals, therefore, add potash or soda, stir, and filter; the iron is thrown out: boil the filtrate, and filter; the chromium is thrown out: neutralize the filtrate by acid, and then add ammonia; the aluminium is thrown out. Note, however, that ferric hydrate will prevent hydrate of chromium being dissolved by potash or soda if the ferric hydrate is in considerable excess. Before concluding that chromium is entirely absent, the 4th reaction should be performed. The hydrates of iron, chromium, and aluminium are insoluble in ammonia, and may therefore be easily separated from the hydrates of the somewhat analogous metals zinc, cobalt, nickel, and manganese.

Fourth Analytical Reaction.—Add a salt of chromium (either of the above precipitates of chromic oxide or the dry residue of the evaporation of a few drops of a solution of a chromium salt) to a few grains of nitre and carbonate of sodium on platinum foil, and fuse the mixture in the blowpipe-flame; a yellow mass of chromate of potassium and sodium ($KNaCrO_4$) is formed. Dissolve the mass in water, add acetic acid to decompose excess of carbonate, and apply the reagents for chromates.

This is a delicate and useful reaction if carefully performed.

TIN.

Symbol Sn. Atomic weight 117.7.

Source.—The chief ore of tin is stannic oxide (SnO_2), occurring in veins under the name of *tinstone*, or in alluvial deposits as *stream-tin*. The oldest mines are those of Cornwall. Much tin is now imported from Australia.

Preparation.—The metal is obtained by reducing the roasted and washed ore by charcoal or anthracite* coal at a high temperature, and is purified by slowly heating, when the pure tin, fusing first, is run off, a somewhat less fusible alloy of tin with small quantities of arsenicum, copper, iron, or lead remaining. The latter is known as *block tin;* the former heated till brittle and then hammered or let fall from a height splits into prismatic fragments, resembling starch or columnar basalt, and is named *dropped* or *grain tin*. Good tin emits a crackling noise in bending, termed the cry of tin, caused by the friction of its crystalline particles on each other.

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* *Anthracite* (from *ἄνθραξ*, *anthrax*, a burning coal) or *stone coal* differs from the ordinary *bituminous* or *caking coal* in containing less volatile matter, and, therefore, in burning without flame. It gives a higher temperature, and from its non-caking properties is, in furnace operations, more manageable than bituminous coal.

Uses.—Tin is an important constituent of such alloys as pewter, Britannia metal, solder, speculum-metal, bell-metal, gun-metal, and bronze. It is very ductile, and may be rolled into plates or leaves, known as *tin foil*, varying from $\frac{1}{250}$ to $\frac{1}{1000}$ of an inch in thickness. Common tin foil, however, usually contains a large proportion of lead. The reflecting surface of *looking-glasses* was, formerly, always an amalgam of tin and mercury, produced by carefully sliding a plate of glass over a sheet of tin foil on which mercury had been rubbed, and then excess of mercury poured; but pure silver, deposited from a solution, is now largely employed. *Pins* are made of brass wire, on which tin is deposited. *Tin plate*, of which common utensils are made, is iron alloyed with tin by dipping the acid-cleansed sheet into melted tin covered with oil, which, by dissolving any trace of oxide, or, perhaps, by preventing oxidation, enables the tin more completely to alloy with the iron. *Tin tacks* are in reality tinned iron tacks; a tin nail would be too soft to drive into wood. Tin may be granulated by melting and triturating briskly in a hot mortar, by shaking melted tin in a box on the inner sides of which chalk has been rubbed, or, in thin little bells or corrugated fragments (Granulated Tin, B. P.), by melting in a ladle and, as soon as fluid, pouring from the height of a few feet into water. Powdered tin has been used medicinally as a mechanical irritant to promote expulsion of worms. The hair of the pods of *Kiwach* or *Cowhage* (Hindustani) (*Mucuna pruriens*, P. I.) is almost the only medicine (excluding diluents and dentifrices) which acts in such a directly mechanical manner.

The chemical position of tin among the metals is close to that of arsenicum and antimony. Its atom is quadrivalent and bivalent. The two classes of salts are termed stannic and stannous respectively. They are all made directly or indirectly from the metal itself.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

Chloride of Tin. Stannous Chloride.

First Synthetical Reaction.—Warm a fragment of tin with hydrochlorous acid; hydrogen escapes and solution of stannous chloride ($SnCl_2$, perhaps Sn_2Cl_4) is formed. It may be retained for future experiments.

One ounce of tin dissolved in three fluidounces of hydrochloric acid and one of water, and the resulting solution diluted to five fluidounces, constitutes the "Solution of the Chloride of Tin."—B. P.

Solid Stannous Chloride.—By evaporation of the above solution stannous chloride is obtainable in crystals ($SnCl_2,2H_2O$). It is a powerful reducing agent, even a dilute solution precipitating gold, silver, and mercury from their solutions, converting ferric and cupric into ferrous and cuprous salts, and partially deoxidizing arsenic, manganic, and chromic acids. It absorbs oxygen from the air, and is decomposed when added to a large quantity of water unless some acid be present. It is used as a mordant in dyeing and calico-printing.

Perchloride of Tin. Stannic Chloride.

Second Synthetical Reaction.—Through a portion of the solution of the stannous chloride of the previous reaction pass chlorine gas; solution of stannic chloride ($SnCl_4$) is formed. Or add hydrochloric acid to the stannous solution, boil, and slowly drop in nitric acid until no more fumes are evolved; again stannic chloride results. Reserve the solutions for subsequent experiments.

Stannic Oxide, or Anhydride, and Stannates.

Third Synthetical Reaction.—Boil a fragment of tin with nitric acid, evaporate to dryness, and strongly calcine the residue; light buff-tinted stannic anhydride (SnO_2) is produced. Heat the stannic anhydride with excess of solid caustic potash or soda; stannate of the alkali metal (K_2SnO_3 or Na_2SnO_3) results. Dissolve the stannate in water, and add hydrochloric acid; white, gelatinous *stannic acid* (H_2SnO_3) is precipitated. Stannic acid is also obtained on adding an alkali to solution of stannic chloride; it is soluble in excess of acid or alkali.

The product of the action of nitric acid on tin is also an acid, but from its insolubility in hydrochloric and other acids is different from ordinary stannic acid. It is termed *metastannic acid* (from *μετὰ*, *meta*, beyond), and probably has a composition expressed by the formula $H_{10}Sn_5O_{15}$. (*Vide* Index, "Isomerism.") It is also produced on gently heating stannic acid:—

$$\underset{\substack{\text{Stannic}\\\text{acid.}}}{5H_2SnO_3} = \underset{\substack{\text{Metastannic}\\\text{acid.}}}{H_{10}Sn_5O_{15}}$$

Metastannates have the general formula $M_2H_8Sn_5O_{15}$. Both acids yield buff-colored stannic oxide or anhydride (SnO_2) when strongly heated. The latter is employed in polishing plate under the name of *putty powder*. *Stannate of sodium* ($Na_2SnO_3,4H_2O$) is used as a mordant by dyers and calico-printers under the name of *tin prepare-liquor*.

(*b*) *Reactions having Analytical Interest* (*Tests*).

Stannous or Stannic Salts.—Heat any solid tin compound with a mixture of cyanide of potassium and carbonate of sodium on charcoal by the inner flame of the blowpipe. Globules of tin separate, having, when cut by a knife, characteristic brightness and hardness.

STANNOUS SALTS.

First Analytical Reaction.—Through a dilute solution of a stannous salt (stannous chloride, for example; see previous page) pass sulphuretted hydrogen gas; brown stannous sulphide (SnS) is precipitated. Pour off the supernatant liquid, add ammonia to the moist precipitate (to neutralize acid), and lastly yellow sulphydrate of ammonium solution; the precipitate is dissolved.

Aqueous solution of sulphydrate of ammonium becomes yellow when a day or two old, and then contains excess of sulphur, that element having become displaced by oxygen absorbed from the air; hence, in the above reaction, the stannous sulphide (SnS), in dissolving, becomes stannic sulphide (SnS_2); for the latter is precipitated on decomposing the alkaline liquid by an acid.

Second Analytical Reaction.—To solution of a stannous salt add solution of potash or soda; white stannous hydrate falls ($Sn2HO$). Add excess of the alkali; the precipitate dissolves. Boil the solution; some of the tin is precipitated as blackish stannous oxide (SnO).

Ammonia gives a similar precipitate, insoluble in excess. The alkaline carbonates do the same, carbonic acid gas escaping.

STANNIC SALTS.

Third Analytical Reaction.—Through a solution of a stannic salt (stannic chloride, for example; see page 239) pass sulphuretted hydrogen gas; yellow stannic sulphide (SnS_2) is precipitated. Pour off the supernatant liquid, and to the moist precipitate add ammonia (to neutralize acid), and then sulphydrate of ammonium; the precipitate dissolves.

Note.—In precipitating stannic sulphide the presence of too much hydrochloric acid must be avoided; the formation of the precipitate is also facilitated if the solution be warmed. Stannic sulphide, like the sulphide of arsenicum and antimony, dissolves in a solution of alkaline sulphide or sulphydrate, with formation of definite crystallizable sulphostannates (M'_2SnS_3).
Anhydrous stannic sulphide, prepared by sublimation, has a yellow or orange lustrous appearance, and is used by decorators as *bronzing-powder*. It is sometimes termed *mosaic gold*.

Fourth Analytical Reaction.—To solution of a stannic salt add potash or soda; white stannic acid falls (H_2SnO_3). Add excess of the alkali; the precipitate dissolves. Boil the mixture; no reprecipitation occurs—a fact enabling stannic to be distinguished from stannous salts.

Ammonia gives a similar precipitate, soluble, but not readily, in excess. The fixed alkali-metal carbonates do the same, carbonic acid gas escaping; after a time the stannic salt is again deposited, probably as stannate of the alkali metal. Carbonate of ammonium and acid carbonates of alkali metals give a precipitate of stannic acid insoluble in excess.

Antidotes.—In cases of poisoning by tin salts (dyer's tin liquor, *e. g.*), solution of carbonate of ammonium should be given. White of egg is also said to form an insoluble precipitate with compounds of tin. Vomiting should be speedily induced, and the stomach-pump quickly applied.

GOLD.

Symbol Au. Atomic weight 196.2.

Source.—Gold occurs in the free state in nature, occasionally in nodules or *nuggets*, but commonly in a finer state of division termed *gold dust.*

Preparation.—Gold is separated from the sand, crushed quartz, or other earthy matter with which it may be associated, by agitation with water, when the gold, from its relatively greater specific gravity, falls to the bottom of the vessel first, the lighter mineral matter being allowed to run off with the water. From this rich sand the gold is dissolved out by mercury, the amalgam filtered, and afterwards distilled, when the mercury volatilizes and gold remains. The amalgamation may be much facilitated by the use of a small proportion of sodium, as already described in treating of silver.

Pure gold is too soft for general use as a circulating medium. *Gold coin* is an alloy of copper and gold, that of Great Britain containing 1 of the former to 11 of the latter, or 8⅓ per cent. of copper, that of France, Germany, and the United States about 10 per cent. *Jeweller's gold* varies in quality, every 24 parts containing 18, 15, 12, or 9 parts of gold, the alloys being technically termed 18, 15, 12, or 9 *carat fine.* Articles made of the better qualities are usually stamped by authority. Trinkets of inferior intrinsic worth are commonly thinly coated with pure gold by electro-deposition or otherwise. *Gold leaf* (U. S. P.), is nearly pure gold passed between rollers till it is about $\frac{1}{800}$ of an inch in thickness and then hammered between sheets of animal membrane, termed gold-beater's skin and calf-skin vellum, till it is $\frac{1}{160000}$ or $\frac{1}{200000}$ of an inch in thickness. It may even be hammered till 280,000 leaves would be required to form a pile an inch thick.

Gold Coinage.—The weight of gold is expressed in Great Britain in ounces troy and decimal parts of an ounce, and the metal is always taken to be of standard fineness (11 gold and 1 alloy) unless otherwise described. The degree of fineness of gold, as ascertained by assay, is expressed decimally, fine pure gold ("gold free from metallic impurities," B. P.) being taken as unity, or 1.000. Thus gold of British standard is said to be 0.9166 fine, of French standard 0.900 fine. The legal weight of the sovereign is 0.2568 ounce of standard gold, or 123.274 grains. The weight came from one pound of standard gold (5760 grains) being coined into 44½ guineas. Gold coins are legal tender to any amount, provided that the weight of each sovereign does not fall below 122.5 grains, or in the case of a half sovereign 61.125 grains; these are the "least current" weights of the coins.

Note.—In chemical analysis gold comes out among the sulphides of the metals precipitated by sulphuretted hydrogen; and of those sulphides, it, like the sulphides of tin, antimony, and arsenicum, is soluble in sulphydrate of ammonium.

Quantivalence.—Gold is trivalent (Au'''), but in some compounds univalent (Au').

Reactions.

Synthetical Reactions.—Place a fragment of gold (*e. g.*, gold leaf) in ten or twenty drops of aqua regia (a mixture of three parts of nitric and four or five of hydrochloric acid), and set the test-tube aside in a warm place; solution of perchloride of gold or auric chloride ($AuCl_3$) results. When the metal is dissolved, evaporate nearly to dryness to remove most of the excess of fluid, dilute with water, and retain the solution for subsequent experiments. Sixty grains of gold treated thus, and the resulting chloride dissolved in five ounces of distilled water, constitute "Solution of Chloride of Gold," B. P.

$$Au_2 + 2HNO_3 + 6HCl = 2AuCl_3 + 2NO + 4H_2O.$$

This reaction has analytical interest also; for in examining a substance suspected to be or contain metallic gold, solution would have to be effected in the above way before reagents could be applied. Gold is insoluble in hydrochloric, nitric, and the weaker acids.

Chloride of Gold and Sodium (*Auri et Sodii Chloridum*, U. S. P.) is "a mixture composed of equal parts of dry chloride of gold and chloride of sodium."

Analytical Reactions (*Tests*).

First Analytical Reaction.—Through a few drops of solution of an auric salt (the chloride, $AuCl_3$, is the only convenient one) pass sulphuretted hydrogen; brown auric sulphide (Au_2S_3) is precipitated. Filter, wash, and add yellow sulphydrate of ammonium solution; the precipitate dissolves.

Second Analytical Reaction.—To solution of a salt of gold add ferrous chloride or sulphate, and set the tube aside; metallic gold is precipitated, a ferric salt remaining in solution.

This is a convenient way of preparing pure gold, or *fine gold* as it is termed, or of working up the gold residues of laboratory operations. The precipitate, after boiling with hydrochloric acid, washing and drying, may be obtained in a button by mixing with an equal weight of borax or acid sulphate of potassium and fusing in a good furnace.

Third Analytical Reaction.—Add a few drops of dilute solutions of stannous and stannic chloride to a considerable quantity of distilled water; pour the liquid, a small quantity at a time, in a very dilute solution of auric chloride ($AuCl_3$), well stirring; the mixture assumes a purple tint, and flocks of a precipitate known as the *Purple of Cassius* (from the name of the discoverer, M. Cassius) are produced.

The same compound is formed on immersing a piece of tin foil in solution of auric chloride; it is said to be a mixture of auric, aurous, stannic, and stannous oxides. It is the coloring agent in the finer varieties of ruby glass.

PLATINUM.

Symbol Pt. Atomic weight 194.4.

Source.—Platinum, like gold, usually occurs in nature in the free state, the chief sources of supply being Mexico, Brazil, and Siberia. It is separated from the alluvial soil by washing.

Uses.—The chief use of platinum is in the construction of foil, wire, crucibles, spatulas, capsules, evaporating-dishes, and stills for the use of the chemical analyst or manufacturer. It is tolerably hard, fusible with very great difficulty, not dissolved by hydrochloric, nitric, or sulphuric acid, and only slightly affected by alkaline substances. It is attacked by aqua regia, with production of perchloride of platinum or platinic chloride ($PtCl_4$). It forms fusible alloys with lead and other metals, and with phosphorus a phosphide, which easily melts. Neither of these substances, therefore, nor mixtures which may yield a metal, should be heated in platinum vessels.

The chemical position of platinum among the elements is close to that of gold. Its atom is quadrivalent in some compounds, in others apparently bivalent (Pt''). The higher salts are termed *platinic*, the lower *platinous*.

The specific gravity of platinum is 21.5; and that of iridium, an allied metal, 22.4.

REACTIONS.

Perchloride of Platinum. Platinic Chloride.

Synthetical Reaction.—Place a fragment of platinum in a little aqua regia and set the vessel aside in a warm place, adding more acid from time to time if necessary; solution of perchloride of platinum ($PtCl_4$) results. Evaporate the solution to remove excess of acid, and complete the desiccation over a water-bath. Dissolve the residue in water, and retain the solution for subsequent experiments, and as a reagent for the precipitation of salts of potassium and ammonium.

A quarter of an ounce of platinum treated in the above manner, and the resulting chloride dissolved in five ounces of water, constitutes "Solution of Perchloride of Platinum," B. P., or 1 part of pure platinic chloride ($PtCl_4,5H_2O$) dissolved in 20 of distilled water gives "Test Solution of Platinic Chloride," U. S. P.

This reaction has analytical interest also; for in examining a substance suspected to be or to contain metallic platinum, solution would have to be thus effected before reagents could be applied.

Analytical Reactions (*Tests*).

First Analytical Reaction.—Through a few drops of a solution of a platinic salt ($PtCl_4$ is the only convenient one), to which an equal quantity of solution of chloride of sodium has been added, pass sulphuretted hydrogen; dark-brown platinic sulphide (PtS_2) is precipitated. Filter, wash, and add sulphydrate of ammonium; the precipitate dissolves.

If chloride of sodium be not present in the above reaction, the precipitated sulphide will contain platinous chloride, and may detonate if heated.

Second Analytical Reaction.—Add excess of solution of carbonate of sodium and some sugar to solution of perchloride of platinum and boil; a precipitate of metallic platinum falls.

Platinum Black is the name of this precipitate. It possesses in a high degree a quality common to many substances, but largely possessed by platinum, namely, that of absorbing or occluding gases. In its ordinary state, after well washing and drying, it absorbs from the air and retains many times its bulk of oxygen. A drop of ether or alcohol placed on it is rapidly oxidized, the platinum becoming hot. This action may be prettily shown by pouring a few drops of ether into a beaker (one having portions of the top and sides broken off answers best), loosely covering the vessel with a card, and suspending within the beaker a platinum wire, one end being attached to the card by passing through its centre, the other terminating in a short coil or helix near the surface of the ether; on now warming the helix in a flame and then rapidly introducing it into the beaker, it will become red hot, and continue to glow so long as there is ether in the vessel. In this experiment real combustion goes on between the ether vapor and the concentrated oxygen of the air, the products of the oxidation revealing themselves by their odor.

Third Analytical Reaction.—To solution of perchloride of platinum add solution of chloride of ammonium; a yellow granular precipitate of double chloride of platinum and ammonium ($PtCl_4,2AmCl$) falls. When slowly formed in dilute solutions, the precipitate is obtained in minute orange prisms.

Chloride of potassium (KCl) gives a similar precipitate ($PtCl_4$-$2KCl$). Platinic chloride having been stated to be a test for potassium and ammonium salts, the reader is prepared to find that potassium and ammonium salts are tests for platinic salts. The double sodium compound ($PtCl_4 2NaCl$) is soluble in water.

Collect the precipitate, dry, and heat in a small crucible; it is decomposed, and metal, in the finely divided state of *spongy platinum*, remains.

$$3(PtCl_4 2NH_4Cl) = Pt_3 + 2NH_4Cl + 16HCl + 2N_2.$$

Heat decomposes the potassium salt into $Pt + 2KCl + Cl_4$, the chlorine escaping and the chloride of potassium remaining with the platinum.

In working up the platinum residues of laboratory operations, the mixture should be dried, burnt, boiled successively with hydrochloric acid, water, nitric acid, water, then dissolved in aqua regia, excess of acid removed by evaporation, chloride of ammonium added, the precipitate washed with water, dried, ignited, and the resulting spongy platinum retained or converted into perchloride for use as a reagent for alkali metals. It is by this process that the native platinum is treated to free it from the rare metals palladium, rhodium, osmium, ruthenium, and iridium. The spongy platinum is converted into the massive condition by a refinement on the blacksmith's process of *welding* (German *wellen*, to join), or by fusing in a flame of pure oxygen and hydrogen gases, the oxyhydrogen blowpipe.

Occlusion by Spongy Platinum.—Spongy platinum has great power of occlusion. A small piece held in a jet of hydrogen causes ignition of the gas, owing to the close approximation of particles of oxygen (from the air) and hydrogen. Döbereiner's lamp is constructed on this principle—the apparatus being essentially a vessel in which hydrogen is generated by the action of diluted sulphuric acid on zinc, and a cage for holding the spongy platinum.

CADMIUM.

Symbol Cd. Atomic weight 111.8.

In most of its chemical relations cadmium (*Cadmium*, U. S. P.) resembles zinc. In nature it occurs chiefly as an occasional constituent of the ores of that metal. In distilling zinc containing cadmium, the latter, being the more volatile, passes over first. In analytical operations, cadmium, unlike zinc, comes down among the metals precipitated by sulphuretted hydrogen; that is, its sulphide is insoluble in dilute hydrochloric acid, while sulphide of zinc is soluble. It is a white malleable metal nearly as volatile as mercury. Sp. gr. 8.7.

Beyond the occasional employment of the sulphide as a pigment (*jaune brillant*), and the iodide in photography and medicine, cadmium and its salts are but little used. The atom of cadmium is bivalent (Cd'').

Reactions.

Iodide of Cadmium.

First Synthetical Reaction.—Digest together in a flask metallic cadmium, water, and iodine until the color of the iodine disappears; solution of iodide of cadmium (*Cadmii Iodidum*, B. P.) (CdI_2) remains. Pearly micaceous crystals may be obtained on evaporating the solution.

This is the process alluded to in the British Pharmacopœia. The salt is also employed, with other iodides, in iodizing collodion for photographic purposes. It melts when heated, and is soluble in water or spirit, the solution reddening litmus-paper.

Sulphate of Cadmium.

Second Synthetical Reaction.—Dissolve cadmium in nitric acid; pour the resulting solution of nitrate of cadmium ($Cd2NO_3$) into a solution of carbonate of sodium; dissolve the precipitate of carbonate of cadmium ($CdCO_3$) in dilute sulphuric acid, separate and crystallize. Sulphate of cadmium ($CdSO_4$) is a white crystalline salt soluble in water.

First Analytical Reaction.—Through solution of a cadmium salt (CdI_2 or $CdCl_2$) pass sulphuretted hydrogen; a yellow precipitate of sulphide of cadmium (CdS) falls, resembling in appearance arsenious, arsenic, and stannic sulphides. Add sulphydrate of ammonium; the precipitate, unlike the sulphides just mentioned, does not dissolve.

Sulphides of cadmium and copper may be separated by solution of cyanide of potasssium, in which sulphide of copper is soluble and sulphide of cadmium insoluble.

Second Analytical Reaction.—To a cadmium solution add solution of potash; white hydrate of cadmium (Cd2HO) is precipitated, insoluble in excess of the potash.

Hydrate of zinc (Zn2HO), precipitated under similar circumstances, is soluble in solution of potash; the filtrate from the hydrate of cadmium may therefore be tested for any zinc occurring as an impurity by applying the appropriate reagent—sulphydrate of ammonium.

Before the blowpipe-flame, on charcoal, cadmium salts give a brown deposit of oxide of cadmium (CdO).

BISMUTH.

Symbol Bi. Atomic weight 210.

Source.—Bismuth occurs in the metallic state in nature. It is freed from adherent quartz, etc. by simply heating, when the metal melts, runs off, and is collected in appropriate vessels. It is also met with in combination with other elements. Bismuth is grayish-white, with a distinct pinkish tinge.

Uses.—Beyond the employment of some of its compounds in medicine, bismuth is but little used. Melted bismuth expands considerably on solidifying, and hence is valuable in taking sharp impressions of dies. It is a constituent of some kinds of type-metal and of pewter-solder.

The position of bismuth among the metals is close to that of arsenicum and antimony. Its atom is rarely quinquivalent (Bi^{V}), but in most compounds trivalent (Bi''').

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Reactions having Synthetical Interest.*

Nitrate of Bismuth.

First Synthetical Reaction.—To a few drops of nitric acid and an equal quantity of water in a test-tube add a little powdered bismuth, heating the mixture if necessary; nitric oxide (NO) escapes, and solution of *nitrate of bismuth* ($Bi3NO_3$) results.

$$\underset{\text{Bismuth.}}{Bi_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Nitrate of bismuth.}}{2(Bi3NO_3)} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

The solution evaporated gives crystals ($Bi3NO_3,5H_2O$), any arsenicum which the bismuth might contain remaining in the mother-liquor. Native bismuth commonly contains arsenicum, most of which is removed by roasting or by fusing two or three times with a tenth of its weight of nitre, or, finally, by converting the metal into oxynitrate, as described in the next reaction, and reducing this with charcoal at a high temperature.

To make *nitrate* of bismuth and other salts on a larger scale, 2 ounces of the metal, in small fragments, are gradually added to a mixture of 4 fluidounces of nitric acid and 3 of water, and, when effervescence (due to escape of nitric oxide) has ceased, the mixture is heated for ten minutes, poured off from any insoluble matter, evaporated to 2 fluidounces to remove excess of acid, and then either set aside for *crystals* to form, or poured into a half gallon of water to form the *oxynitrate* of bismuth, or into a solution of 6 ounces of carbonate of ammonium in a quart of water to form the *oxycarbonate*, as described in the following reactions. The precipitates should be washed with cold water and dried at a temperature not exceeding 150° F. Exposed in the moist state to 212° for any length of time, they undergo slight decomposition.

Subnitrate or Oxynitrate of Bismuth.

Second Synthetical Reaction.—Pour some of the above solution of nitrate into a considerable quantity of water; decomposition occurs, and oxynitrate of bismuth ($BiONO_3$) in a hydrous state ($BiONO_3,H_2O$) (*Bismuthi Subnitras*, U. S. P.) is precipitated:—

$$\underset{\substack{\text{Nitrate of}\\ \text{bismuth.}}}{Bi3NO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Oxynitrate of}\\ \text{bismuth.}}}{BiONO_3} + \underset{\text{Nitric acid.}}{2HNO_3}$$

Filter, and test the filtrate for bismuth by adding excess of carbonate of sodium; a precipitate shows that some bismuth remains in solution. The following equation, therefore, probably more nearly represents the decomposition:—

$$\underset{\substack{\text{Nitrate of}\\ \text{bismuth.}}}{5(Bi3NO_3)} + \underset{\text{Water.}}{8H_2O} = \underset{\substack{\text{Oxynitrate of}\\ \text{bismuth.}}}{4(BiONO_3,H_2O)} + \underset{\substack{\text{Nitrate of bismuth}\\ \text{in acid.}}}{Bi3NO_3;8HNO_3}$$

Decomposition of nitrate of bismuth by water is the process of the Pharmacopœia for the preparation of oxynitrate or "subnitrate" of bismuth for use in medicine. For this purpose the original metal must contain no arsenicum. In manufacturing the compound, therefore, before pouring the solution of nitrate into water, the liquid should be tested for arsenicum by one of the hydrogen tests; if that element be present, the solution must be evaporated and only the deposited crystals be used in the preparation of the oxynitrate. For on pouring an arsenical solution of nitrate of bismuth into water, the arsenicum is not wholly removed in the supernatant liquid, unless the oxynitrate be redissolved and reprecipitated several times, according to the amount of arsenicum present.

Subnitrate of bismuth is gradually decomposed by solution of alkaline carbonates; also by the bicarbonates, with production of carbonic acid gas, oxycarbonate of bismuth and nitrate of the alkali-metals being formed. It is used as a cosmetic under the name of *Pearl-white* (*Blanc de Perle*).

Oxysalts of Bismuth—It will be noticed that the formula for subnitrate of bismuth ($BiNO_4$) does not accord with that of other nitrates, the characteristic elements of which are NO_3. Analogy would seem to indicate, however, that the fourth atom of oxygen has different functions from the three in the NO_3; for on pouring solution of chloride of bismuth ($BiCl_3$) into water, oxychloride is produced ($BiOCl$) (a white powder used as a cosmetic, also in enamels, and in some varieties of sealing-wax). The bromide ($BiBr_3$) and iodide (BiI_3) similarly treated yield oxybromide ($BiOBr$) and oxyiodide ($BiOI$). The subnitrate ($BiNO_4$) is, therefore, probably an analogous compound, an oxynitrate ($BiONO_3$). The sulphate (Bi_23SO_4) also decomposes when placed in water, giving what may be termed an oxysulphate ($Bi_2O_2SO_4$).

It is difficult to prove whether or not the water in the "subnitrate" or hydrous oxynitrate of bismuth ($BiONO_3,H_2O$) is an integral part of the salt. If it is, the compound is simply the hydrato-nitrate ($BiNO_32HO$) of bismuth.

Oxide of Bismuth.

Third Synthetical Reaction.—Boil subnitrate of bismuth with solution of soda for a few minutes; it is converted into yellowish oxide of bismuth (Bi_2O_3) (*Bismuthi Oxidum*, B. P.).

$2BiONO_3$	+	$2NaHO$	=	Bi_2O_3	+	$2NaNO_3$	+	H_2O
Oxynitrate of bismuth.		Hydrate of sodium.		Oxide of bismuth.		Nitrate of sodium.		Water.

Subcarbonate or Oxycarbonate of Bismuth.

Fourth Synthetical Reaction.—To solution of nitrate of bismuth add carbonate of ammonium or carbonate of sodium; a white precipitate of hydrous oxycarbonate ($2Bi_2O_2CO_3,H_2O$) (*Bismuthi Subcarbonas*, U. S. P.) falls.

$2(Bi3NO_3)$	+	$3Na_2CO_3$	=	$6NaNO_3$	+	$Bi_2O_2CO_3$	+	$2CO_2$
Nitrate of bismuth.		Carbonate of sodium.		Nitrate of sodium.		Oxycarbonate of bismuth.		Carbonic acid gas.

This compound may be regarded as similar in constitution to the oxysalts just described. In Bi_2CO_5 one scarcely recognizes the characteristic elements of carbonates; but considering the preparation to be an oxycarbonate ($Bi_2O_2CO_3$), its relations to carbonates and oxides are evident. These subsalts may all be viewed as normal bismuth salts in which an atom of oxygen displaces an equivalent proportion of other acidulous atoms or radicals:—

Chloride	$Bi3Cl$	Oxychloride . .	$BiOCl$
Bromide	$Bi3Br$	Oxybromide . .	$BiOBr$
Iodide	$Bi3I$	Oxyiodide . .	$BiOI$
Nitrate	$Bi3NO_3$	Oxynitrate . .	$BiONO_3$
Sulphate	Bi_23SO_4	Oxysulphate . .	$Bi_2O_2SO_4$
Carbonate (unknown)	Bi_23CO_3	Oxycarbonate .	$Bi_2O_2CO_3$

They may be viewed, in short, as salts in process of conversion to oxide; continue the substitution a little further, and each yields oxide of bismuth (Bi_2O_3). They have also been considered to be salts of a hypothetical univalent radical, bismuthyl (BiO).

Citrate of Bismuth.

Fifth Synthetical Reaction.—Heat ten parts of oxynitrate of bismuth, seven of citric acid crystals, and thirty to forty of water together for a few minutes, until a drop of the mixture forms a clear solution with ammonia-water. Dilute the crystalline mass with eight to ten times its volume of water, and set aside for a short time to let the citrate deposit; decant the clear liquid. Wash the crystalline sediment three or four times in a similar manner, drain and dry, either on a water-bath or by mere exposure. The yield is 13⅔ parts, showing that the salt is anhydrous, and that its formula is $BiC_6H_5O_7$ (Rother). This is the *Bismuthi Citras*, U. S. P.

Sixth Synthetical Reaction.—Mix citrate of bismuth with water, add sufficient solution of ammonia to form a clear liquid, filter if necessary, evaporate to a syrupy consistence, spread on glass plates, and dry slowly until pearly scales are obtained. This is the *Bismuthi et Ammonii Citras*, U. S. P.

(*b*) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—Through solution of a bismuth salt (a slightly acid solution of nitrate, for example) pass sulphuretted hydrogen; a black precipitate of sulphide of bismuth (Bi_2S_3) falls. Add ammonia (to neutralize acid), and then sulphydrate of ammonium; the precipitate, unlike As_2S_3 and Sb_2S_3, is insoluble.

Second Analytical Reaction.—Concentrate almost any acid solution of a bismuth salt and pour into water; a white salt is precipitated.

This reaction is characteristic of bismuth salts; it has already been amply explained. The precipitate is distinguished from one formed by antimony under similar circumstances by being insoluble in solution of tartaric acid.

Third Analytical Reaction.—To a solution of a bismuth salt add an alkali; hydrate of bismuth ($Bi3HO$) is precipitated, insoluble in excess.

Fourth Analytical Reaction.—A small quantity of the following reagent, including both supernatant liquid and precipitated scales, is transferred to a test-tube and gradually heated until solution takes place. Any liquid containing or supposed to contain bismuth is then added, and the whole allowed to cool. The separated scales will show a distinct change in color to dark orange or crimson according to the quantity of bismuth present.

The *test-reagent* may be prepared by adding to a boiling solution of acetate of lead (half a grain to the ounce) solution of iodide of potassium in considerable excess. The solution of the iodide of lead precipitated is assisted by a little acetic acid. On cooling, iodide of lead is deposited in the characteristic scales.

The reader is again advised to trace out the exact nature of each of the foregoing reactions, chiefly by aid of equations or diagrams.

QUESTIONS AND EXERCISES.

343. Enumerate the fifteen metals, salts of which are frequently employed in pharmacy.

344. Mention the twelve rarer metals interesting to pharmacists.

345. Name the sources and official compounds of lithium.

346. Give an equation explanatory of the formation of Citrate of Lithium.

347. What is the strength of *Liquor Lithiæ Effervescens?*

348. On what chemical hypothesis are lithium compounds administered to gouty patients?

349. Describe the relation of lithium to other metals.

350. What is the chief test for lithium?

351. Write a paragraph on strontium, its natural compounds, chemical relations, technical applications, and tests.

352. What are the formulæ and properties of oxalate of cerium?

353. Name the commonest ores of manganese, and give an equation descriptive of its reaction with hydrochloric acid.

354. Explain the formation of permanganate of potassium, employing diagrams or equations.

355. In what manner do the manganates of potassium act as disinfectants?

356. What are the chief tests for manganese?

357. What are the chief uses of the compounds of cobalt?

358. How are salts of cobalt analytically distinguished from those of nickel?

359. Mention an application of nickel in the arts.

360. What is the general color of nickel salts?

361. State the method of preparation of red chromate of potassium.

362. Give the formulæ of red and yellow chromates of potassium.

363. How is red chromate of potassium obtained?

364. Describe the action of sulphuretted hydrogen on acidified solutions of chromates.

365. What is the formula of chrome alum?

366. Mention the chief tests for the chromic radical, and for chromium.

367. How would you detect iron, chromium, and aluminium in a solution?

368. Define the terms tinstone, stream-tin, block-tin, grain-tin, tin-plate.

369. Describe the position occupied by tin in relation to other metals.

370. What is the difference between stannic acid and metastannic acid?

371. State the applications of tin in the arts.

372. Mention the chief tests for stannous and stannic salts.

373. Name the best antidote in cases of poisoning by tin solution.

374. How is gold dust separated from the earthy matter with which it is naturally associated?

375. How much pure gold is contained in English coin and in jeweller's gold?

376. State the average thickness of gold leaf.

377. What is the weight of a sovereign?

378. Explain the term "fineness" as applied to gold.

379. What effect is produced on gold by hydrochloric, nitric, and nitro-hydrochloric acids respectively?

380. By what reagents is metallic gold precipitated from solutions of its salts?

381. How is Purple of Cassius prepared?

382. Whence is platinum obtained?

383. Why are platinum utensils peculiarly adapted for use in chemical laboratories?

384. How is perchloride of platinum prepared?

385. Name the chief tests for platinum.

386. What is "platinum black"?

387. Describe an experiment demonstrative of the large amount of attraction for gases possessed by metallic platinum.

388. How is "spongy platinum" produced?

389. By what process may the metal be recovered from platinum residues?

390. What is *occlusion* in chemistry?

391. In what condition does cadmium occur in nature?

392. By what process may Iodide of Cadmium be prepared? and in what form is it used in medicine?

393. Mention the chief test for cadmium.

394. Distinguish sulphide of cadmium from other sulphides of similar color.

395. How is cadmium separated from zinc?

396. How does bismuth occur in nature?

397. What is the quantivalence of bismuth?

398. Write down equations descriptive of the actions of nitric acid on bismuth, and water on nitrate of bismuth.

399. How may pure salts be prepared from bismuth containing arsenicum?

400. Give a diagram of the process for the so-called Carbonate of Bismuth.

401. Write formulæ showing the accordance in composition of the official Subnitrate and Carbonate with the other salts of Bismuth, and with ordinary Nitrates and Carbonates.

402. How is *Bismuthi et Ammonii Citras* prepared?

403. What are the tests for Bismuth?

Practical Analysis.

Bismuth is the last of the metals whose synthetical or analytical relations are of general interest. The position of the rarer among the common metals, and the influence which either has on the other during the manipulations of analysis, will now be considered. These objects will be best accomplished, and a more intimate acquaintance with all the metals be obtained, by analyzing, or studying the methods of analyzing, solutions containing one or more metallic salts.

Of the following Tables, the first (1) includes directions for the analysis of an aqueous or only slightly acid solution, containing but one salt of any of the metals hitherto considered. Here the color of the precipitate or precipitates afforded by a metal under given circumstances must largely be relied on in attempting the detection of the various elements.

The folded Table (2) is intended as a chart for the analysis of solutions containing salts of more than one of the common and rarer metals. It is simply a compilation from the foregoing reactions—an extension of the scheme for the analysis of salts of the ordinary metals. Hence it often may be altered or varied in arragement to suit the requirements of the analyst.

That on p. 255 is a mere outline of the other two Tables. It gives the position of the metals in relation to each other, and will much aid the memory in recollecting that relation.

The analysis of solutions containing only one metal will, as already stated, serve to impress the memory with the characteristic tests for the various metals and other radicals, and familiarize the mind with chemical principles. Medical students seldom have time to go further than this. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of bodies as are met with in actual practice, beginning with solutions which may contain any or all of the members of a group (see previous pages), then examining solutions containing more than one group, and finally analyzing liquids in which are dissolved several salts of any of the common or rarer metals.

The Author cannot too strongly recommend students thoroughly to master the art of analysis, not only on account of its direct value, but because its practice enables the learner rapidly and soundly to acquire a good knowledge of chemistry, and greatly to improve his general mental faculties.

1. TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF **ONE** OF THE ELEMENTS HITHERTO CONSIDERED—THE COMMON AND RARER METALS.

Add hydrochloric acid.

<table>
<tr>
<td rowspan="6">Precipitate
Hg(ous) Pb Ag.
Collect, wash, and add AmHO.
Hg ppt., blackened.
Pb ppt., still white.
Ag ppt., dissolved.
Sb and Bi may also be precipitated by HCl, but are dissolved on adding more HCl.</td>
<td colspan="6">If HCl gave no precipitate the metal is still in the liquid; pass H_2S through the solution.</td>
</tr>
<tr>
<td rowspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi As
Sb Sn Au Pt.
Collect wash, add AmHS.
Insoluble | Soluble.
Cd, yellow. | As(ous & ic) Sn(ic) } yellow.
Cu Hg(ic) Pb Bi } black. | Sb, orange.
Sn(ous) Au Pt } black.
Apply special tests for each to the original solution. For these, see the previous pages.</td>
<td colspan="5">If H_2S gave no precipitate add AmCl, AmHO, and AmHS.</td>
</tr>
<tr>
<td rowspan="4">Precipitate
Zn Mn Co Ni Al
Fe Cr.
Zn Al } white.
Cr, green.
Mn, skin-tint.
Ni Co Fe } black.
Test specially for each in original solution. See previous pages.</td>
<td colspan="4">If AmHS gave no precipitate add Am_2CO_3.</td>
</tr>
<tr>
<td colspan="2">Precipitate
Ba Sr Ca.
Collect, wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4.</td>
<td colspan="2">If Am_2CO_3 gave no precipitate add Am_2HAsO_4.</td>
</tr>
<tr>
<td rowspan="2">Ppt.
Ba.</td>
<td>Sol.
Sr Ca
Add dil. H_2SO_4.</td>
<td rowspan="2">Ppt.
Mg.</td>
<td rowspan="2">If no precipitate, test original solution in flame on loop of Pt wire.
L, crimson.
Na, yellow.
K, violet.
If neither, test orig. sol. for Am.</td>
</tr>
<tr>
<td>Ppt. Sol.
Sr.—Ca.</td>
</tr>
</table>

2. TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF ANY OF THE COMMON OR RARER METALS.

[*To face page* 254.

Add hydrochloric acid.

<table>
<tr><td colspan="3">Precipitate
Hg(ous) Pb Ag.
Wash, boil with water, filter.</td><td colspan="20">Filtrate
Cd Cu Hg(ic) Pb Bi As(ous)(ic) Sb Sn(ous)(ic) Zn Mn Co Ni Al Fe(ous)(ic) Cr Ba Ca Sr Mg L K Na Am.
Pass H_2S through the liquid, filter.</td></tr>
<tr><td colspan="2">Precipitate
Hg(ous) Ag.
Wash, add AmHO.</td><td rowspan="2">Filtrate
Pb.
Add H_2SO_4.
White ppt.</td><td colspan="8">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn.
Collect, wash, digest in AmHS, filter.</td><td colspan="12">Filtrate
Zn Mn Co Ni Al Fe Cr Ba Ca Sr Mg L K Na Am.
Add AmCl, AmHO, AmHS, warm gently and filter.</td></tr>
<tr><td>Ppt.
Hg(ous).
Black ppt.</td><td>Filtrate
Ag
Add HNO_3.
White ppt.</td><td colspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi.
Wash, boil in HNO_3, filter.</td><td colspan="3">Filtrate
As Sb Sn.
Add dilute HCl, filter, drain well, add *strong* HCl, boil, dilute slightly, filter.</td><td colspan="6">Precipitate
Zn Mn Co Ni Al Fe Cr.
Collect, wash, dissolve in HCl with a few drops of HNO_3, boil, add AmHO, stir, filter.</td><td colspan="6">Filtrate
Ba Ca Sr Mg L K Na Am.
Add Am_2CO_3, warm, filter.</td></tr>
<tr><td colspan="3" rowspan="4">See also p. 256.</td><td rowspan="3">Ppt.
Hg (ic).
Black.
Confirm by Cu test in original solution.</td><td colspan="4">Filtrate
Cd Cu Pb Bi.
Add AmHO, filter.</td><td rowspan="3">Insol.
As.
Yellow.
Confirm by Fleitmann's test.</td><td colspan="2">Filtrate
Sn Sb.
Pour into H-apparatus.</td><td colspan="3">Precipitate *
Fe Al Cr.
Wash, dry, fuse on foil with Na_2CO_3 and KNO_3, boil in water and filter.</td><td colspan="3">Filtrate
Zn Mn Co Ni.
Acidify with $HC_2H_3O_2$, pass H_2S, filter.</td><td colspan="3">Precipitate
Ba Sr Ca.
Collect, wash, dissolve in $HC_2H_3O_2$, add excess of K_2CrO_4, filter.</td><td colspan="3">Filtrate
Mg L K Na Am.
Add Am_2HAsO_4, stir, filter.</td></tr>
<tr><td colspan="2">Precipitate
Pb Bi.
Wash, add a few drops HNO_3, dilute, filter.</td><td colspan="2">Filtrate
Cd Cu.
Add KCy and H_2S.</td><td rowspan="2">Sn
remains on Zn.
Dissolve in HCl and apply tests.</td><td rowspan="2">Sb
escapes as SbH_3.
Test as usual.</td><td rowspan="2">Residue
Fe_2O_3, brown.
Test original solution for ferrous or ferric state.</td><td colspan="2">Filtrate.
If yellow, Cr present. Divide in two parts.</td><td rowspan="2">Sol.
Mn.
Add AmHO and AmHS.
Pink, turning brown.
Search also for Mn in the Fe Al Cr ppt.</td><td colspan="2">Precipitate
Zn Co Ni.
Boil with HCl and a little HNO_3; add KHO, filter.</td><td rowspan="2">Ppt.
Ba.
Yellow.</td><td colspan="2">Filtrate
Sr Ca.
Add dilute H_2SO_4, let stand, filter.</td><td rowspan="2">Ppt.
Mg.</td><td colspan="2">Filtrate
L K Na Am.
Evaporate to small bulk. Add AmHO.</td></tr>
<tr><td>Ppt.
Bi.</td><td>Filt.
Pb.
Dilute, add H_2SO_4, set aside.
White ppt.</td><td>Ppt.
Cd.
Yellow.</td><td>Filt.
Cu.
Acidify with $HC_2H_3O_2$.
Brown ppt.</td><td>Sol.
Al.
Add AmCl, warm and filter.
White ppt.</td><td>Sol.
Cr.
Add $HC_2H_3O_2$ and excess of $AgNO_3$; red ppt.
Or boil with H_2SO_4 and spirit.
Green solution.</td><td>Filt.
Zn
AmHS.
White ppt.</td><td>Precipitate
Co Ni.
Dissolve in HCl, and proceed as directed on pp. 233.</td><td>Ppt.
Sr.</td><td>Filt.
Ca.
Add $Am_2C_2O_4$.
White ppt.</td><td>Ppt.
L.</td><td>Filtrate
K Na Am.
Evaporate, ignite, dissolve.
K by $PtCl_4$,
Na by flame.
Am in original solution.</td></tr>
<tr><td colspan="5">See also pp. 256–257.</td><td colspan="3">See also pp. 256–257.
Au and Pt are specially sought when necessary.</td><td colspan="3">See also pp. 256–257.
* Test this also for Mn, by Crum's process, p. 230.</td><td colspan="3"></td><td colspan="3">See also p. 257.</td><td colspan="3"></td></tr>
</table>

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3. OUTLINE OF THE ANNEXED ANALYTICAL TABLES.

HCl	H_2S		AmHS.		Am_2CO_3	Am_2HAsO_4	
Hg (as mercurous salt)	Cd	Insoluble in AmHS.	Zn	Hydrates soluble in AmHO.	Ba	Mg	K
	Cu						
Pb (partially)	Hg (as mercuric salt)		Mn*		Sr		Na
			Co		Ca		Am
Ag	Pb (entirely)		Ni				
	Bi						
			Al	Hydrates insol. in AmHO.			
	As (as arsenious or arsenic salt)	Soluble in AmHS.	Fe				L
	Sb						
	Sn (as stannous or stannic salt)		Cr				
	Au						
	Pt						

* See page 229.

The laboratory student should practise the examination of aqueous solutions of salts of the above metals until able to analyze with facility and acuracy.

GENERAL AND SPECIAL MEMORANDA RELATING TO THE PRECEDING ANALYTICAL TABLES.

General Memoranda.

These charts are constructed for the analysis of salts more or less soluble in water.——The student has still to learn how substances insoluble in water are to be brought into a state of solution; but, once dissolved, their analysis is effected by the same scheme as that just given. The Tables, especially the second (No. 2), may therefore be regarded as fairly representing the method by which metallic constituents of chemical substances are separated from each other and recognized.——The methods of isolation of the complementary constituent of the salt (the reactions of non-metals and acidulous radicals) will form the next object of practical study.

The general memoranda given in connection with the first Table (p. 219) are equally applicable to the extended second Table, and should again be carefully read through.

Special Memoranda.

The hydrochloric-acid precipitate may at first include some antimony and bismuth as oxychlorides, readily dissolved, however, by excess of acid.——If either of these elements be present, the washings of the precipitate will probably be milky; in that case add a few drops of hydrochloric acid, which will clear the liquid and make way for the application of the test for lead.

The sulphuretted-hydrogen precipitate may be white, in which case it is nothing but sulphur; for, as already indicated, ferric salts are reduced to ferrous, and chromates to the lower salts of chromium by sulphuretted hydrogen, sulphur being deposited:—

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2;$$
$$4H_2CrO_4 + 6H_2S + 12HCl = 2Cr_2Cl_6 + 16H_2O + 3S_2.$$

But the precipitate may also be colored, or even white when only lead or mercury is present, through an insufficiency of sulphuretted hydrogen having produced a peculiar oxysulphide or hydrato-sulphide. The gas should be passed through the liquid until, even after well shaking, it smells strongly of sulphuretted hydrogen.

The portion of the sulphuretted-hydrogen precipitate dissolved by sulphydrate of ammonium may include a trace of copper, sulphide of copper being not altogether insoluble in sulphydrate of ammonium.——On adding hydrochloric acid to the sulphydrate-of-ammonium solution, a white precipitate of sulphur only may be produced, the sulphydrate of ammonium nearly always containing free sulphur.——Strong hydrochloric acid does not readily dissolve small quantities of sulphide of antimony out of much sulphide of arsenicum; and, on the other hand, the strong hydrochloric acid takes into solution a small quantity of sulphide of arsenicum if much sulphide of antimony is present. The precipitate or the original solution should therefore be examined by the other (hydrogen) tests for these elements if doubt exists concerning the presence or absence of either. Tin remains in the hydrogen-bottle in the metallic state, deposited as a black powder on the zinc used in the experiment. The contents of the bottle are turned out into a dish, ebullition continued until evolution of hydrogen ceases, and the zinc is taken up by the excess of sulphuric acid employed; any tin is then filtered out, washed, dissolved in a few drops of hydrochloric acid, and the liquid tested for tin by the usual reagents. ——Tin may be detected in the mixed sulphides of tin, arsenicum, and antimony by the blowpipe reaction (*vide* Index).

The portion of the sulphuretted-hydrogen precipitate not dissolved by the sulphydrate of ammonium may leave a yellow semi-fused globule of sulphur on boiling with nitric acid. This globule may be black, not only from presence of mercuric sulphide, but also from inclosed particles of other sulphides protected by the sulphur from the action of the acid. It may also contain sulphate of lead, produced by the action of nitric acid on sulphide of lead. In cases of doubt the mass must be removed from the liquid, boiled with nitric acid till dissolved, the solution evaporated to remove excess of acid, and the residue examined; but usually it may be disregarded. ——Before testing for bismuth, any considerable excess of acid should be removed by evaporation, and the residual liquid should be freely diluted. If no precipitate (oxynitrate of bismuth) appear, chloride-of-ammonium solution may be added, oxychloride of bismuth more readily forming than even oxynitrate.——Or any nitric acid or sulphuric acid having been neutralized by ammonia, hydrochloric acid is added, and then iodide of potassium; a rich orange color results if bismuth be present.——In testing for lead by sulphuric acid the liquid should be diluted and set aside for some time.

Mercury may also be isolated by digesting the sulphuretted-hydrogen precipitate in sulphydrate of sodium instead of sulphydrate of ammonium. The sulphides of arsenicum, antimony, tin, and mercury are thus dissolved out. The mixture is then filtered, excess of hydrochloric acid added to it, and the precipitated sulphides collected on a filter, washed, and digested in sulphydrate of ammonium; sulphide of mercury remains insoluble, while the sulphides of arsenicum, antimony, and tin are dissolved. By this method copper also appears in its right place only, sulphide of copper being quite insoluble in sulphydrate of sodium. The other metals are then separated in the usual way.

The sulphydrate-of-ammonium precipitate may, if the original solution was acid, contain Phosphates, Oxalates, Silicates, and Borates of Barium, Calcium, and Magnesium. These will subsequently come out with the iron, and, being white, give the iron precipitate a light-colored appearance; their examination must be conducted separately, by a method described subsequently in connection with the treatment of substances insoluble in water.——The precipitates containing aluminium, iron, and chromium hydrates often contain some manganese. This manganese may be detected by washing the hydrates to remove all traces of chlorides, boiling with nitric acid, adding either puce-colored oxide of lead or red lead, and setting the vessel aside. If manganese be present a red or purple liquid is produced.——Sulphide of nickel is not easily removed by filtration (*vide* p. 232) until most of the excess of sulphydrate of ammonium has been dissipated by prolonged ebullition.

The carbonate-of-ammonium precipitate may not contain the whole of the barium, strontium, and calcium in the mixture, unless free ammonia be present; for the carbonates of those metals are soluble in water charged with carbonic acid. If, therefore, the liquid is not distinctly ammoniacal, solution of ammonia should be added. ——Neither carbonate nor hydrate of ammonium wholly precipitates magnesian salts; and, as a partial precipitation is undesirable, a solvent, in the form of an alkaline salt (chloride of ammonium), if not already in the liquid, should be added.——In the chart opposite p. 254 strontium is ordered to be separated from calcium by adding to the acetic solution diluted sulphuric acid. The latter, unless extremely dilute, may precipitate calcium. Any such loss of calcium is in itself of little consequence, because enough sulphate of calcium remains in the filtrate to afford a calcium reaction when ammonia and oxalate of ammonium are subsequently added. But the calcium precipitated by the sulphuric acid may be wrongly set down as strontium. Therefore test a little of the acetic solution for strontium by an aqueous solution of sulphate of calcium, when, if no precipitate falls after setting aside for several minutes, strontium may be regarded as absent. If a precipitate occurs strontium is present; the rest of the acetic solution is then tested for calcium as directed in the chart, the final testing by oxalate of ammonium being, of course, preceded by the addition of ammonia.

Lithium.—The search for lithium may usually be omitted. Should a precipitate, supposed to be due to lithium, be obtained, it must be tested in a flame (= scarlet tint), as a little magnesium not unfrequently shows itself under similar circumstances.

Spectral Analysis.—If present only in minute proportions, the lithium may also remain with the alkalies; it can then only be detected by physical analysis (by a prism) of the light emitted from a tinged flame—by, in short, an instrument termed a spectroscope. Such a method of examination is called spectral analysis, a subject of much interest and of no great difficulty, but scarcely within the range of Pharmaceutical Chemistry; it will be briefly described in connection with the methods of analyzing solid substances.

QUESTIONS AND EXERCISES.

404. Describe a general method of analysis by which the metal of a single salt in a solution could be quickly detected.

405. Give illustrations of black, white, light pink, yellow, and orange sulphides.

406. Mention the group-tests generally employed in analysis.

407. Under what circumstances may a hydrochloric precipitate contain antimony or bismuth?

408. If a sulphuretted-hydrogen precipitate is white, what substances are indicated?

409. Give processes for the qualitative analysis of liquids containing the following substances:—

a. Arsenicum and Cadmium.
b. Bismuth and Antimony.
c. Ferrous and Ferric salts.
d. Aluminium, Iron, and Chromium.
e. Arsenicum, Antimony, and Tin.
f. Lead and Strontium.
g. Iron, Sodium, and Arsenicum.
h. Mercury, Manganese, and Magnesium.
i. Zinc, Manganese, Nickel, and Cobalt.
j. Barium, Strontium, and Calcium.

THE ACIDULOUS RADICALS.

Introduction.—The twenty-seven radicals which have up to this point mainly occupied attention are (admitting ammonium, NH_4) metals; and they have been almost exclusively studied not in the free state, but in the condition in which they exist in salts. Moreover, these metals have been treated as if they formed the more important constituent, the stronger half, the foundation or *base* of salts. Attention has been continuously directed to the metallic or *basylous* side of salts. And indeed there is still one more basylous radical which must be mentioned, though it is usually supposed to play only a subordinate part in medicine—Hydrogen. Unlike the salts of most metals, those of hydrogen (the so-called acids) are never, in medicine or the arts generally, professedly used for the sake of their hydrogen, but always for the other half of the salt, the *acidulous* side. And it is not for their basylous radical that these hydrogen salts are now commended to notice,* but in order to study, under the most favorable circumstances, those acidulous groupings which have continually presented themselves in operations on salts, but which were for the time of secondary importance. These *acidulous radicals* may now be treated as the primary object of attention; and there is no better way of doing so than in operating on their compounds with hydrogen, the relatively inferior medicinal importance of which element, as compared with potassium, iron, and other basylous radicals, will serve to give the desired prominence to the *acidulous radicals* in question.

Common Acids.—These salts of hydrogen (hydrogen easily displaceable, or in certain cases, in part, by ordinary metals) are the ordinary sharp, sour bodies termed *acids* (from the Latin root *acies*, an edge). The following Table includes the formulæ and usual names of the most important; others will be noticed subsequently. A few of those mentioned are unstable or somewhat rare; in such cases a common metallic salt containing the acidulous radical may be used for reactions.

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* It must not be forgotten that the commonest salt of any radical whatsoever is a salt of hydrogen, the oxide of hydrogen (H_2O), or hydrate of hydrogen (HHO), *water*. In the reactions already performed the value of this compound has been constantly recognized, both for its hydrogen and for its oxygen, but most of all as the vehicle or medium by which nearly all other atoms are enabled to come into that contact with each other without which their existence would be almost useless; for some atoms are like some animals—out of water they are as inactive as fishes. It is true that both fishes and salts have usually to be removed from water to be utilized by man; but before they can be assimilated, either as food or as medicine, they must again seek the agency of water in becoming dissolved.

HCl	hydrochloric acid.
HBr	hydrobromic acid.
HI	hydriodic acid.
HCN (HCy)	hydrocyanic acid.
HNO_3	nitric acid.
$HClO_3$	chloric acid.
$HC_2H_3O_2$	acetic acid.*
H_2S	hydrosulphuric acid.†
H_2SO_3	sulphurous acid.
H_2SO_4	sulphuric acid.
H_2CO_3?	carbonic acid.
$H_2C_2O_4$	oxalic acid.
$H_2C_4H_4O_6$	tartaric acid.
$H_3C_6H_5O_7$	citric acid.
H_3PO_4	phosphoric acid.
H_3BO_3	boracic acid.

The old names are here retained for these acids, but, in studying their chemistry and chemical relations to other salts, they are usefully spoken of by such more purely chemical names as (for hydrochloric acid) chloride of hydrogen, (for nitric acid) nitrate of hydrogen, and so on—sulphate of hydrogen, tartrate of hydrogen, phosphate of hydrogen.

A prominent point of difference will at once be noticed between the basylous radicals met with up to the present time and the acidulous groupings included in the above tabular list. The former are nearly all elements, ammonium only being a compound; the latter are mostly compounds, chlorine, bromine, iodine, and sulphur being the only elements. This difference will not, however, be so apparent when the chemistry of alcohols, ethers, and such bodies has been mastered, for they are all salts of *compound* basylous radicals.

Rarer Acids.—The above acids contain the only acidulous groupings that commonly present themselves in analysis or in pharmaceutical operations. There are, however, several other acids (such as hypochlorous, nitrous, hypophosphorous, valerianic, benzoic, gallic, tannic, uric, hyposulphurous, hydroferrocyanic, hydroferridcyanic, lactic, etc.) with which it is desirable to be more or less familiar; reactions concerning these will therefore be described. Arsenious, arsenic, stannic, manganic, and chromic acids have already been treated of in connection with the metals they contain; in practical analysis they always become sufficiently altered to come out among the metals.

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* The hydrogen on the acidulous side must not be confounded with the basylous hydrogen in all these hydrogen salts or acids; the two perform entirely different functions. Hydrogen in the acidulous portion is like the hydrogen in the basylous radical ammonium: it has combined with other atoms to form a group which plays more or less the part of an elementary radical, and to which a single symbol is not unfrequently applied (Am; Cy, $\bar{A}$, O, T, C, etc.). Cobalt, chromium, iron, platinum, etc., resemble hydrogen in this respect in often uniting with other atoms to form definite acidulous radicals, in which the usual basylous character of the metals has for the time disappeared. In *hydrides* (p. 121) hydrogen itself is an acidulous radical.

† Synonyms: sulphydric acid and sulphuretted hydrogen.

Quantivalence.—A glance at the foregoing Table is sufficient to show the quantivalence of the acidulous radicals. The first seven are clearly univalent, then follow six bivalent, leaving three trivalent.

These all combine with equivalent amounts of basylous radicals to form various salts; hence they may be termed monobasylous, dibasylous, and tribasylous radicals. The acids themselves were formerly spoken of as monobasic, dibasic, and tribasic respectively, or monobasic and polybasic, in reference to the amount of *base* (hydrates or oxides) they could decompose; but the terms are no longer definite, and hence but little used in mineral chemistry.

Antidotes.—The antidotes in cases of poisoning by the strong acids will naturally be non-corrosive alkaline substances, as soap and water, magnesia, common washing "soda," or other carbonates. Vinegar, lemon-juice, and weak or non-corrosive acids would be the appropriate antidotes to caustic alkalies.

Analysis.—The practical study of the acidulous side of salts will occupy far less time than the basylous. Salts will then be briefly examined as a whole.

One Word of Caution.—It is only for convenience in the division of chemistry for systematic study that salts may be considered to contain basylous and acidulous radicals, or separate sides, so to speak; for we possess no absolute knowledge of the internal arrangement of the atoms (admitting that there are such things) in the molecule of a salt. We only know that certain groups of atoms may be transferred from compound to compound in mass (that is, without apparent decomposition); hence the assumption that these groups are radicals. A salt is probably, however, a whole, having no such sides as those mentioned.

QUESTIONS AND EXERCISES.

410. Mention the basylous radical of acids.

411. Give illustrations of univalent, bivalent, and trivalent acidulous radicals, or monobasylous, dibasylous, and tribasylous radicals.

412. What is the difference between an elementary and a compound acidulous radical?

413. Name the grounds on which salts may be assumed to contain basylous and acidulous radicals.

HYDROCHLORIC ACID AND OTHER CHLORIDES.

Formula of Hydrochloric Acid HCl. Molecular weight* 36.4.

The acidulous radical of hydrochloric acid and of other chlorides is the element chlorine (Cl). It occurs in nature chiefly as chloride of sodium (NaCl), either solid, under the name of *rock-salt*, mines of which are not unfrequently met with, or in solution in the water of all seas. Common table-salt is more or less pure chloride of sodium in minute crystals. Chlorine, like hydrogen, is univalent (Cl'); its atomic weight is 35.4. Its molecule is symbolized thus, Cl_2, chloride of chlorine.

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* The weight of a molecule is the sum of the weights of its atoms.

REACTIONS.

Hydrochloric Acid.

First Synthetical Reaction.—To a few fragments of chloride of sodium in a test-tube or small flask add about an equal weight of sulphuric acid; colorless and invisible gaseous hydrochloric acid is evolved, a sulphate of sodium remaining. Adapt to the mouth of the vessel by a perforated cork a piece of glass tubing bent to a right angle, heat the mixture, and convey the gas into a small bottle containing a little water; solution of hydrochloric acid results.

$$\underset{\text{Chloride of sodium.}}{NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Acid sulphate of sodium.}}{NaHSO_4}$$

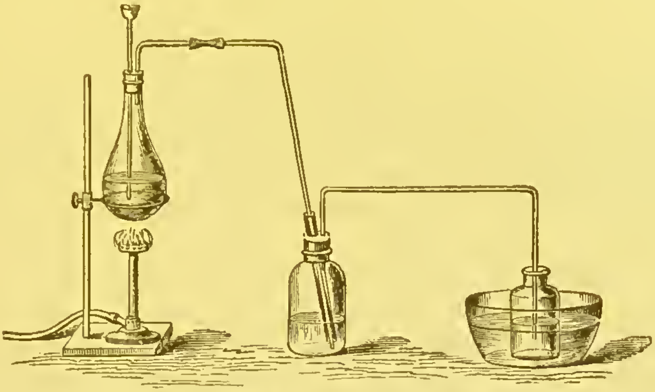
Hydrochloric Acid.—The product of this operation is the nearly colorless and very sour liquor commonly called hydrochloric acid. When of certain given strengths (estimated by volumetric analysis) it forms *Acidum Hydrochloricum*, U. S. P. (*Acidum Muriaticum*), and *Acidum Hydrochloricum Dilutum*, U. S. P. The former has a specific gravity of 1.16 and contains 31.9 per cent. of real acid. The latter, specific gravity 1.049, with 10 per cent. of the real acid, is made by diluting 6 fluid parts of the strong acid with 13 of water. The above process is that of the manufacturer, larger vessels being employed, and the gas being freed from any trace of sulphuric acid by washing. Other chlorides yield hydrochloric acid when heated with sulphuric acid; but chloride of sodium is always used, because cheap and common.

Common yellow hydrochloric acid is a by-product in the manufacture of carbonate of sodium from common salt, a process in which the chloride of sodium is first converted into sulphate, hydrochloric acid being liberated. This impure acid is liable to contain iron, arsenic, fixed salts, sulphuric acid, sulphurous acid, nitrous compounds, and chlorine.

The process for the preparation of hydrochloric acid is as follows: it may be carried out by the student with about one-twelfth of the quantities mentioned:—

"Take of chloride of sodium, dried, 48 ounces, sulphuric acid 44 fluidounces, water 36 fluidounces, distilled water 50 fluidounces; pour the sulphuric acid slowly into 32 ounces of the water, and, when the mixture has cooled, add it to the chloride of sodium previously introduced into a flask having the capacity of at least one gallon. Connect the flask by corks and a bent glass tube with a three-necked wash-bottle, furnished with a safety-tube, and containing the remaining 4 ounces of the water [or let the flask-tube pass loosely through a wider tube fixed in the cork of the wash-bottle, as shown in Fig. 37]; then, applying heat to the flask, conduct the disengaged gas through the wash-bottle into a second bottle containing the distilled water, by means of a bent tube dipping about half an inch below the surface, and let the process be continued until the product measures 36 ounces, or the liquid has acquired a specific gravity of 1.16. The bottle containing the distilled water must be kept cool during the whole operation."

Fig. 37.



Preparation of Hydrochloric Acid.

The modification of wash-bottle shown in the figure allows of the easy insertion or removal of a delivery-tube. The wider tube there shown, or an ordinary tube-funnel, also acts as a *safety-tube* by admitting air the moment there is any tendency in the water in the receiver to be forced back on account of a too rapid absorption of the gas. The time of the student will be saved if hydrochloric acid already in stock be placed in the wash-bottle instead of water.

Invisible gaseous hydrochloric acid forms visible grayish-white fumes on coming into contact with air. This is due to combination with the moisture of the air. The intense greediness of hydrochloric gas and water for each other is strikingly demonstrated on opening a test-tube full of the gas under water; the latter rushes into and instantly fills the tube. If the water is tinged with blue litmus, the acid character of the gas is prettily shown at the same time. The test-tube, which should be perfectly dry, may be filled from the delivery-tube direct; for the gas is somewhat heavier than, and therefore readily displaces, air. The mouth may be closed by the thumb of the operator. At low temperatures hydrochloric acid and water form a crystalline compound, $HCl,2H_2O$.

Note.—The process includes the use of as much sulphuric acid as is theoretically necessary for the production of acid sulphate of sodium ($NaHSO_4$), which remains in the generating vessel. A hot solution of this residue carefully neutralized by carbonate of sodium, filtered and set aside, yields normal sulphate (*Sodii Sulphas*, U. S.

P.), "Glauber's Salt," in the form of transparent oblique efflorescent prisms ($Na_2SO_4,10H_2O$).

$$\underset{\substack{\text{Acid sulphate}\\\text{of sodium.}}}{2NaHSO_4} + \underset{\substack{\text{Carbonate of}\\\text{sodium.}}}{Na_2CO_3} = \underset{\substack{\text{Sulphate of}\\\text{sodium.}}}{2Na_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

Chlorine.

Second Synthetical Reaction.—To some drops of hydrochloric acid (that is, the common aqueous solution of the gas) add a few grains of black oxide of manganese, and warm the mixture; *chlorine*, the acidulous radical of all chlorides, is evolved, and may be recognized by its peculiar odor or irritating effect on the nose and air-passages.

$$4HCl + MnO_2 = Cl_2 + 2H_2O + MnCl_2.$$

Chlorine-water.—This is the process of the Pharmacopœia for the production of chlorine-water (*Aqua Chlori*, U. S. P.), the gas being first washed and then passed into water. Chlorine slowly decomposes water, with production of hydrochloric acid and oxygen gas; it is best preserved in a green-glass well-stoppered bottle in a cool and dark place. At common temperatures (60° F.), if fresh and thoroughly saturated, chlorine-water contains more than twice (2.3) its bulk of chlorine, or less than 1 per cent. (about 0.75) by weight. Chlorine passed into cold water yields crystals of hydrous chlorine ($Cl\,5H_2O$), and these when heated under pressure give an upper layer of chlorine-water and a lower layer of *liquid chlorine.*

Note.—To obtain the chlorine from other chlorides, sulphuric acid as well as black oxide of manganese must be added. Hydrochloric acid is first formed. The action described in the foregoing equation then goes on, except that half instead of the whole of the oxygen of the black oxide is available for the removal of the hydrogen from the chlorine of the hydrochloric acid, the other half being taken up by the hydrogen of the sulphuric acid. Thus, supposing common salt to be the chloride used, the following equations may represent the supposed steps of the process:—

$$\begin{array}{lllll} & 2NaCl + H_2SO_4 & = Na_2SO_4 & + 2HCl, & \\ & MnO_2 + H_2SO_4 & = MnSO_4 & + H_2O & + O; \\ \text{then the} & 2HCl + O & = H_2O & + Cl_2 & \end{array}$$

or the whole may be included in one equation:—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

This reaction may have occasional analytical interest, a very small quantity of combined chlorine being recognized by its means. But the following test is nearly always applicable for the detection of this element, and leaves nothing to be desired in point of delicacy.

Analytical Reactions (Test).

To a drop of hydrochloric acid, or to a dilute solution of any other chloride, add solution of nitrate of silver; a white curdy precipitate falls. Pour off most of the supernatant liquid, add nitric acid and boil; the precipitate does not dissolve. Pour off the acid, and add dilute ammonia; the precipitate quickly dissolves. Neutralize the solution by an acid; chloride of silver is once more precipitated.

The formation of this white precipitate, its appearance, insolubility in boiling nitric acid, solubility in ammonia and in solution of its carbonate and reprecipitation by an acid, form abundant evidence of the presence of chlorine. Its occurrence as a chloride of a metal is determined by testing for the metal with the appropriate reagent; its occurrence as hydrochloric acid is considered to be indicated by the odor, if strong, and the sour taste, if weak, of the liquid, and the action of the liquid on blue litmus-paper, which, like other acids, it reddens. If hydrochloric acid be present in excessive quantity, it will, in addition to the above reactions, give rise to strong effervescence on the addition of a carbonate, a chloride being formed. The chlorine in insoluble chlorides, such as calomel, "white precipitate," etc., may be detected by boiling with caustic potash, filtering, acidulating the filtrate by nitric acid, and then adding the nitrate of silver.

Antidotes.—In cases of poisoning by strong hydrochloric acid, solution of carbonate of sodium (common washing soda) or a mixture of magnesia and water may be administered as an antidote.

QUESTIONS AND EXERCISES.

414. A specimen of official Hydrochloric Acid contains 31.8 per cent. by weight of gas, and its specific gravity is 1.16; work out a sum showing what volume of it will be required, theoretically, to mix with black oxide of manganese for the production of one gallon of chlorine-water, one fluidounce of which contains 2.66 grains of chlorine. *Ans.* 5½ fluidounces, nearly (5.4).

415. Why does hydrochloric acid gas give visible fumes on coming into contact with air?

416. How much chloride of sodium will be required to furnish one pound of chlorine?

417. Give the analytical reactions of chlorides.

418. What antidotes may be administered in cases of poisoning by hydrochloric acid?

HYDROBROMIC ACID AND OTHER BROMIDES.

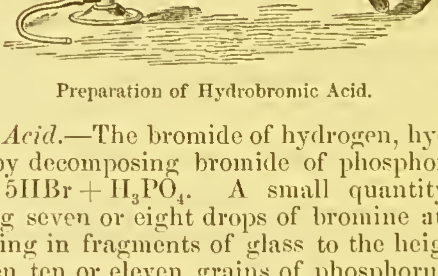
Formula of Hydrobromic Acid HBr. Molecular weight 80.8.

Bromine: Source, Preparation, and Properties.—The acidulous radical of hydrobromic acid and other bromides is the element bromine, Br (*Bromum*, U. S. P.). It occurs in nature chiefly as bromide of magnesium ($MgBr_2$) in sea-water and certain saline springs, and is commonly prepared from the *bittern*, or residual liquors of salt-works. It may be liberated from its compounds by the process for chlorine from chlorides—that is, by heating with black oxide of manganese and sulphuric acid (see page 264). It is a dark-red volatile liquid, emitting an odor more irritating, if possible, than chlorine—of specific gravity 2.990, boiling-point 145.4° F.

Test of purity, U. S. P.—If 3 gm. of Bromine be mixed with 30 c.c. of water and enough water of ammonia to render the solution colorless, the liquid then digested with carbonate of barium, filtered, evaporated to dryness, and the residue gently ignited, the latter [chiefly bromide of barium] should be soluble in absolute alcohol without leaving more than 0.26 gm. of residue [chloride of barium] (abs. of more than 3 per cent. of chlorine). If an aqueous solution of Bromine be poured upon reduced iron and shaken with the latter until it has become nearly colorless, then filtered, mixed with gelatinized starch, and a few drops of Bromine solution be now carefully poured on top, not more than a very faint blue zone should appear at the line of contact of the two liquids (limit of iodine).

Quantivalence.—The atom of bromine, like that of chlorine, is univalent (Br'). The atomic weight of bromine is 79.8. Free bromine has the molecular formula Br_2, bromide of bromine.

Fig. 38.



Preparation of Hydrobromic Acid.

Hydrobromic Acid.—The bromide of hydrogen, hydrobromic acid, may be made by decomposing bromide of phosphorus by water—$PBr_5 + 4H_2O = 5HBr + H_3PO_4$. A small quantity may be prepared by placing seven or eight drops of bromine at the bottom of a test-tube, putting in fragments of glass to the height of about an inch or two, then ten or eleven grains of phosphorus, then another inch of glass, and finally a couple of inches of glass fragments slightly wetted with water, a delivery-tube being fitted on by a cork. The phosphorus combines readily, almost violently, with the bromine as soon as the vapor of the latter, aided by a little warmth from a flame, rises to the region of the phosphorus. The bromide of phosphorus thus formed then suffers decomposition by the water of the moist glass, phosphoric and phosphorous acids being produced. The hydrobromic acid gas passes over (heat being applied in the after part of the operation), and may be condensed in water or in solution of ammonia. The latter solution on evaporation yields bromide of ammonium.

Other Methods.—One hundred parts of sodium hyposulphite, fifty of bromine, and ten of water, are placed in a flask and the generated gas is conducted into the upper portion of 140 parts of water contained in another vessel. When the gas begins to come over slowly, gentle heat is applied. The product is nearly 190 parts of liquid containing 25 per cent. of real acid; specific gravity 1.204. It should be kept in a cool dark place (*Hager*). *Squibb* prefers to decompose solution of bromide of potassium by sulphuric acid, and, after removal of potassium sulphate by crystallization, to distil the residual fluid. *Wade* prescribes an almost pure clear solution of the acid made by shaking together 120 grains of bromide of potassium and 153 grains of crystallized tartaric acid in 1 ounce of distilled water, and setting aside till precipitation of acid tartrate of potassium ceases. *Goebel* decomposes bromide of barium by an equivalent weight of sulphuric acid; preparing the bromide of barium by heating a wet mixture of bromide of ammonium and carbonate of barium until carbonate of ammonium fumes cease to be evolved. *Fletcher* prefers to pass sulphuretted hydrogen gas through water containing bromine, and, when all bromine has disappeared, distilling the mixture. The distillate, when diluted until it has a sp. gr. of 1.300, contains 34 per cent. of HBr.

$$10Br_2 + 4H_2S + 8H_2O = 20HBr + 2H_2SO_4 + S_2.$$

Acidum Hydrobromicum Dilutum, U. S. P., has a sp. gr. of 1.077 and contains 10 per cent. of HBr.

Bromide of Potassium (KBr) is occasionally employed in pharmacy, and is the salt, therefore, which may be used in studying the reactions of this acidulous radical. The official method of making the salt has been alluded to under the salts of potassium (page 76).

Other Bromides are seldom used; they may be prepared in the same way as, and closely resemble, the corresponding chlorides or iodides. *Bromide of Sodium* (*Sodii Bromidum*, U. S. P.) crystallizes in anhydrous cubes (NaBr) from solutions at 110° or 120° F., and in hydrous prisms ($NaBr,2H_2O$) at ordinary temperatures.

Bromide of Ammonium (AmBr) (*Ammonii Bromidum*, U. S. P.) is prepared by agitating iron wire with a solution of bromine until the odor of bromine can be no longer perceived, adding solution of ammonia, filtering, and evaporating the filtrate to dryness. It forms a white granular salt, which becomes slightly yellow on exposure to air, is readily soluble in water, less so in spirit, and, when heated, sublimes. Bromide or Iodide of Ammonium may also be made by mixing equivalent quantities of strong hot, aqueous solutions of the corresponding potassium salts and of sulphate of ammonium. To the cooled liquids rectified spirit is added, which precipitates the sulphate of potassium. The spirit recovered by distillation of the clear liquid leaves the required salt as a residue in the retort.

Bromide of Calcium, $CaBr_2$ (*Calcii Bromidum*, U. S. P.), may be prepared by neutralizing hydrochloric acid by hydrate or carbonate of calcium, filtering, and evaporating to dryness; or by uniting bromine with iron, boiling the aqueous solution with lime until the mixture is red, filtering and evaporating. It is a white deliquescent granular salt, soluble in water and in alcohol.

Solution of Bromine, B. P., 10 minims in 5 ounces, is an aqueous solution, bromine being slightly soluble in water.

Hypobromites, *Bromates*, *Perbromates*, analogous to hypochlorites, chlorates, and perchlorates, are producible.

Bromates occurring as an impurity in bromides are detected by dropping diluted sulphuric acid on to the salt, when a yellow color, due to free bromine, is produced *immediately* if bromates are present.

Analytical Reactions (*Tests*).

First Analytical Reaction.—To a few drops of solution of a bromide (KBr, or NH_4Br) add solution of nitrate of silver; a yellowish-white precipitate of bromide of silver (AgBr) falls. Treat the precipitate successively with nitric acid and dilute ammonia, as described for the chloride of silver; it is only sparingly dissolved by the ammonia.

Second Analytical Reaction.—To solution of a bromide add a drop or two of chlorine-water or a bubble or two of chlorine gas; then add a few drops of chloroform or ether, or disulphide of carbon, shake the mixture, and set the test-tube aside; the chlorine, from the greater strength of its affinities, liberates the bromine, which is dissolved by the chloroform or ether, the solution falling to the bottom of the tube in the case of the heavy chloroform, or rising to the top in the case of the light ether. Either solution has a distinct yellow or reddish-yellow or red color, according to the amount of bromine present.

Note.—This reaction serves for the isolation of bromine when mixed with many other substances. Excess of chlorine must be avoided, as colorless chloride of bromine is then formed. Iodides give a somewhat similar but more violet appearance; the absence of iodine must therefore be insured by a process given in the next section. The above solution in chloroform or ether may be removed from the tube by drawing up into a *pipette* (small pipe—a narrow glass tube, usually having a bulb or expanded portion in the centre) the bromide fixed by the addition of a drop of solution of potash or soda, the chloroform or ether evaporated off, and the residue tested as described in the next reaction.

The above operation is frequently employed for synthetical purposes.

Third Analytical Reaction.—Liberate bromine from a bromide by the cautious addition of chlorine or chlorine-water, then add a few drops of cold decoction of starch; a yellow combination of bromine and starch, commonly termed "bromide of starch," is formed.

Decoction of starch is made by rubbing down two or three grains of starch with some drops of cold water, then adding much more water and boiling the mixture.

The above reaction may be varied by liberating the bromine by a little black oxide of manganese and a drop of sulphuric acid, the upper part of the inside of the test-tube being smeared over with some thick decoction of starch or thin starch-paste. Even sulphuric acid alone, if strong, liberates bromine from a bromide, the hydrogen of the hydrobromic acid first produced uniting with the oxygen of the sulphuric acid—the latter being reduced to sulphurous acid or even to hydrosulphuric acid.

HYDRIODIC ACID AND OTHER IODIDES.

Formula of Hydriodic Acid HI. Molecular weight 127.6.

Source.—The acidulous radical of hydriodic acid and other iodides is the element iodine (I). It occurs in nature chiefly as iodide of sodium and of magnesium in sea-water. Seaweeds, sponges, and other marine organisms, which derive much of their nourishment from sea-water, store up iodides in their tissues, and it is from the ashes of these that supplies of iodine (*Iodum*, U. S. P.) are obtained.

Process.—The seaweed ash or *kelp* is treated with water, insoluble matter thrown away, and the decanted liquid evaporated and set aside to allow of the deposition of most of the sulphates, carbonates, and chlorides of sodium and potassium. The residual liquor is treated with excess of sulphuric acid, which causes evolution of carbonic and sulphurous or sulphuretted gases, deposition of sulphur and more sulphate of sodium, and formation of hydriodic acid. To the decanted liquid is added black oxide of manganese, and the mixture is then slowly distilled; the iodine sublimes, and is afterwards purified by re-sublimation.

$$2HI + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + I_2.$$

The analogy of chlorine, bromine, and iodine is well indicated by the fact that each is obtained from its compounds by the same reaction. Iodine is liberated from any iodide as bromine from bromides, or chlorine from chlorides—namely, by the action of black oxide of manganese and sulphuric acid.

Properties.—Iodine is a crystalline purplish-black substance; its vapor, readily seen on heating a fragment in a test-tube, is dark violet. Its vapors are irritating to the lungs; but a trace may be inhaled with safety (*Vapor Iodi*, B. P.). It melts at 239°, boils at about 392° F., and is entirely volatilized, the first portions containing any cyanide of iodine that may be present. The latter body occurs in slender colorless prisms, emitting a pungent odor.

"A solution of Iodine in chloroform should be perfectly clear and limpid (abs. of moisture). When shaken with distilled water, it should not communicate to the latter more than a light brownish tinge, and no deep brown color (abs. of chloride of iodine). If the Iodine be removed from this dilute aqueous solution by agitation with disulphide of carbon, and, after the separation of the latter, some dilute solution of ferrous sulphate with a trace of ferric chloride be added, finally solution of soda, and the whole supersaturated with hydrochloric acid, no blue precipitate should make its appearance (abs. of cyanide of iodine). If Iodine be dissolved in sulphurous acid, the solution strongly supersaturated with ammonia, and completely precipitated by nitrate of silver, the filtrate, on being supersaturated with nitric acid, should not at once become more than faintly cloudy (abs. of more than traces of chlorine or bromine)." U. S. P.

This latter reaction is applied for the detection of chloride or bromide in Iodides, omitting the addition of sulphurous acid.

Quantivalence.—The atom of iodine, like those of bromine and chlorine, is univalent* (I'). The atomic weight of iodine is 126.6, its molecular formula I_2.

The Iodide of Hydrogen, or Hydriodic Acid, is a heavy, colorless gas. Its solution in water may be made by passing sulphuretted hydrogen through water in which iodine is suspended.

$$2H_2S + 2I_2 = S_2 + 4HI.$$

Kolbe prepares hydriodic acid by adding to 10 parts of iodine contained in a flask, in an atmosphere of carbonic acid gas, 1 part of phosphorus, little by little and slowly. On the mixture of di- and tri-iodide of phosphorus are poured 4 parts of water. From this abundance of hydriodic acid is evolved on the application of gentle heat, and it is not contaminated by free iodine. Phosphoric acid remains.

Or iodine may be dissolved in bisulphide of carbon in a tall cylinder, water added, and sulphuretted hydrogen passed through the mixture. The water dissolves the hydriodic acid, the bisulphide retaining the separated sulphur. The aqueous solution only needs boiling for two or three minutes to remove excess of sulphuretted hydrogen.—*Winkler.*

Syrupus Acidi Hydriodici, U. S. P., contains 1 per cent. of real acid.

Iodide of potassium (KI) is largely used in medicine, and hence is the most convenient iodide on which to experiment in studying the reactions of this acidulous radical. Solid iodine itself might be taken for the purpose; but its use and action in that state have already been alluded to in describing the iodides of potassium, cadmium, and mercury; its analytical reactions in the combined condition are those which may now occupy attention.

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* There is a compound of iodine having the formula ICl_3. Iodine would at first sight, therefore, seem to be a trivalent element (I'''); and bromine and fluorine, from their close chemical analogy with iodine, would necessarily be regarded as trivalent also. From this aspect the position of chlorine would be anomalous. Possibly, however, the compound is only a molecular combination of chloride of iodine, ICl, with chlorine, Cl_2. Iodine also forms with iodide of potassium a periodide, or tri-iodide, KI_3, which may be obtained in lustrous prismatic crystals. This, too, may have the formula KI,I_2. A mercuric hexiodide (HgI_6, perhaps HgI_2,I_2,I_2) is also known; and a periodide of ammonium, NH_4I_2,I_2.

Solution of Iodine.—Iodine is slightly soluble in water (iodine-water), and readily soluble in an aqueous solution of iodide of potassium. Five parts of iodine and 10 of iodide of potassium dissolved in 85 of distilled water, form *Liquor Iodi Compositus*, U. S. P. ("Lugol's Solution"); 4 parts of iodine and 1 of iodide of potassium, rubbed with 2 parts of water and 93 of benzoated lard form *Unguentum Iodi*, U. S. P. It is more soluble in spirit (*Tinctura Iodi*, U. S. P.), or in a spiritous solution of iodide of potassium (*Tinctura Iodi*, B. P.). It combines with sulphur, forming an unstable grayish-black solid iodide (S_2I_2), having a radiated crystalline structure (*Sulphuris Iodidum*, U. S. P.). If 100 parts be thoroughly boiled with water, the iodine will pass off in vapor, and about 20 parts of sulphur remain.—*B. P.* and *U. S. P.*

Analytical Reactions (Tests).

First Analytical Reaction.—To a few drops of an aqueous solution of an iodide (*e. g.*, KI) add solution of nitrate of silver; a light yellow precipitate of iodide of silver (AgI) falls. Pour away the supernatant liquid and treat the precipitate with nitric acid, it is not dissolved; pour away the acid and then add dilute ammonia, it is only sparingly dissolved.

This reaction is useful in separating iodine from most other acidulous radicals, but does not distinguish iodine from bromine.

The presence of chloride in iodide of silver may be detected by boiling with dilute solution of carbonate of ammonium, filtering off the insoluble iodide of silver and saturating the filtrate with nitric acid; any chloride of silver is then precipitated.

Ammonia, it will be remembered, dissolves chloride of silver readily; hence the presence of chloride of potassium in bromide or iodide may be detected by dissolving in water, adding excess of nitrate of silver, collecting the precipitate, washing, digesting in ammonia, filtering, and adding excess of nitric acid to the filtrate; a white curdy precipitate indicates a chloride (of potassium). Bromide and iodide of silver are, however, slightly soluble in ammonia. A better process is given on page 273.

Second Analytical Reaction.—Liberate iodine from an iodide by the cautious addition of chlorine, then add cold decoction of starch; a deep-blue combination of iodine and starch, commonly termed "iodide of starch," is formed.

Starch is highly sensitive to the action of iodine; this reaction is consequently very delicate and characteristic. The reaction is not observed in hot liquids. Excess of chlorine must be avoided, or colorless chloride of iodine will be produced. Nitrous acid, or a nitrite acidulated with sulphuric acid, may be used instead of chlorine. Concentrated sulphuric acid also liberates iodine from iodides, the hydrogen of the hydriodic acid first produced uniting with the oxygen of the sulphuric acid—the latter (H_2SO_4) being reduced to sulphurous acid (H_2SO_3) or even to hydrosulphuric acid (H_2S).

In testing bromine for iodine the bromine must be nearly all removed by dilute solution of sulphurous acid before the decoction of starch is added.

Ozone (O_3).—Papers soaked in mucilage of starch containing iodide of potassium form a test for free chlorine and nitrous acid, and are also employed by meteorologists to detect an allotropic or physically polymeric and energetic form of oxygen termed by Schönbein *ozone* (from ὄζω, *ozō*, I smell). This substance liberates iodine from iodide of potassium (with formation of iodide of starch), and is supposed to occur normally in the atmosphere, the salubrity or insalubrity of which is said to be dependent to some extent on the presence or absence of ozone. The possible occurrence of nitrous or chlorinoid gases in the air, however, renders the test untrustworthy. Houzeau proposes to test for ozone by exposing litmus-paper of a neutral tint soaked in a dilute solution of iodide of potassium; the potash set free by action of the ozone turns the paper blue. The same paper without iodide would indicate the extent to which the effect might be due to ammonia vapor. Ozone, or rather ozonized air, is produced artificially in large quantities on passing air through a box (Beane's Ozone-generator) highly charged with electricity. In the latter operation condensation of the volume of air, or, rather, of the oxygen in the air, occurs. Small quantities are obtained by exposing in a loosely closed bottle a stick of phosphorus partially covered by water, but the product is mixed with peroxide of hydrogen. Ozone is a powerful bleaching, disinfecting, and general oxidizing agent; insoluble in water, soluble in oils of turpentine, cinnamon, and some other liquids. From experiments that have been made by Soret on the specific gravity of ozone, its molecular formula would seem to be O_3, that of ordinary oxygen being O_2. Its smell is peculiar. (See p. 235, also "Blood.")

Third Analytical Reaction.—To a neutral aqueous solution of an iodide, add a solution containing one part of sulphate of copper to two and a half parts of green sulphate of iron, and well shake; a dirty-white precipitate of cuprous iodide (Cu_2I_2) falls.

$$2KI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_2 3SO_4.$$

Or to the liquid containing an iodide add the solution of copper sulphate and some solution of sulphurous acid, and warm the mixture, cuprous iodide falls.

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2I_2 + 2KHSO_4 + H_2SO_4.$$

Separation of Chlorides, Bromides, and Iodides.—Chlorides and bromides are not affected in this way; the reaction is useful, therefore, in removing iodine from a solution in which chlorides and bromides have to be sought. The total removal of iodine by the former of the two modifications of the process is insured by supplementing the addition of the cupric and ferrous sulphates by a few drops of solution of potash or soda, any acid which might be keeping cuprous iodide in solution being thereby neutralized, ferric or ferrous hydrate, precipitated at the same time, not affecting the reaction. Occasionally, too, it may be necessary to repeat the process with the filtrate before the last traces of iodine are removed. The second modification of the process is, on the whole, to be preferred.

Chloride of the rare metal palladium performs a similar useful office in removing iodine, but not bromine or chlorine, from solutions.

Chlorides may be separated from bromides by taking advantage of the ready solubility of chloride of silver, and slow and slight solubility of bromide of silver in ammonia, especially in (a fair, not a great, excess of) ammonia containing chloride of silver.

Siebold's test for the detection of chlorides when occurring with bromides is based upon the fact that a strong solution of permanganate of potassium liberates the bromine from moderately strong solutions of bromides containing a large excess of sulphuric acid. A strong solution of permanganate is added to the aqueous solution of bromide or iodide (containing not more than 1 in 40), strongly acidified by dilute sulphuric acid, until the permanganate ceases to be decolorized, and a copious precipitate of oxide of manganese is formed. The mixture is boiled for about five minutes to expel the bromine, and then filtered. The colorless filtrate is now quite free from bromine, and may be tested for chlorine by nitrate of silver. If a chloride be present, a small quantity of its chlorine is lost by this process; but the main portion always remains, provided that no undue excess of the permanganate be used. It is essential, therefore, that the filtrate should be colorless; for if it be colored so as to indicate the presence of undecomposed permanganate, the loss of the greater part if not of the whole of the chlorine must be expected. If, on the other hand, too little permanganate be employed, a trace of bromide may be left in the filtrate. If the solution under examination should be very much stronger than 1 in 40, water should be added before boiling (just after the addition of the permanganate), in order to avoid a loss of HCl.

Chlorides may also be detected in bromides and iodides by taking advantage of the formation of chlorochromic anhydride (page 236) and the non-occurrence of corresponding compounds of bromine or iodine.

To a solution of a chloride with a bromide and an iodide add a concentrated solution of sulphate of sodium, and then a reagent prepared by mixing equal volumes of sulphuric acid and saturated solution of sulphate of copper, until no further precipitation of cuprous iodide occurs. Next add solution of soda to remove excess of sulphate of copper; filter and evaporate to dryness. Place the dried residue, together with an equal bulk of red chromate of potassium, in a dry test-tube fitted with a delivery-tube, or into a small retort, and cover the mixture with sulphuric acid. Distil into water. Chromic anhydride and hydrochloric and hydrobromic acids are liberated by the sulphuric acid, and reacting upon one another form chlorochromic anhydride, together with free bromine and chlorine.

$$CrO_3 + 2HCl = CrCl_2O_2 + H_2O.$$
$$2CrO_3 + 6HCl + 3H_2SO_4 = Cr_23SO_4 + 3Cl_2 + 6H_2O.$$
$$2CrO_3 + 6HBr + 3H_2SO_4 = Cr_23SO_4 + 3Br_2 + 6H_2O.$$

The chlorochromic anhydride is decomposed by the excess of water into which it falls, giving rise to chromic acid, which imparts its color to the liquid, and hydrochloric acid.

$$CrCl_2O_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

The chlorine escapes and the bromine is dissolved by the water. The colored liquid is then shaken with chloroform, which removes the bromine—indicating bromine in the original substance. A yellow color remaining is due to chromic acid, indicating chlorides in the original substance. Or add ammonia to the distillate—the color due to bromine is thereby entirely removed, while that of the chromic compound is only slightly modified.

Fourth Analytical Reaction.—Iodides have been shown to be useful in testing for mercuric salts (see the Mercury reactions, p. 201); a mercuric salt (corrosive sublimate, for example) may therefore be used in testing for iodides, a scarlet precipitate of mercuric iodide (HgI_2) being produced.

This reaction may be employed where large quantities of an iodide are present; but its usefulness in analysis is much impaired by the fact that the precipitate is soluble in excess of the dissolved iodide or in excess of the mercuric reagent. Its color and insolubility in water distinguish it from mercuric chloride, bromide, and cyanide, which are white soluble salts.

Fifth Analytical Reaction.—Iodides have also (see the Lead reactions, p. 211) been shown to be useful in testing for lead salts; similarly a lead salt (acetate, for example) may be used in testing for iodides, a yellow precipitate of iodide of lead (PbI_2), soluble in hot water and crystallizing in yellow scales on cooling, being produced.

Chloride, bromide, and cyanide of lead are white; hence the above reaction may occasionally be useful in distinguishing iodine from the allied radicals. But iodide of lead is slightly soluble in cold water; hence small quantities of iodide cannot be detected by this reaction. (For *Iodates* see p. 293.)

Analogies between Chlorine, Bromine, Iodine, and their Compounds.—These elements form a natural group or family, each distinct from the other, yet closely related. Moreover, their dissimilarities are so curiously gradational as to irresistibly suggest the idea that some day we may find the differences between these bodies to be in degree rather than in kind. Thus chlorine is a gas and iodine a solid, while bromine occupies the intermediate condition. The atomic weight of bromine is nearly midway between those of chlorine and iodine. The same may be said of the weight of equal volumes of each in the gaseous state. The specific gravity of fluid chlorine is 1.33, of iodine 4.95, while bromine is nearly 3. Liquid chlorine is transparent, iodine opaque, bromine intermediate. The crystalline forms of the chloride, bromide, and iodide of a metal are commonly identical. One volume of either element in the gaseous state combines with an equal volume of hydrogen (at the same temperature) to form two volumes of a gaseous acid, very soluble in water (hydrochloric acid, hydrobromic acid, hydriodic acid). Many other analogies are traceable.

QUESTIONS AND EXERCISES.

419. State the method by which Bromine is obtained from its natural compounds.

420. Mention the properties of bromine.

421. How may the Bromides of Potassium and Ammonium be made?

422. By what reagents may bromides be distinguished from chlorides?

423. Whence is iodine obtained?

424. By what process is iodine isolated?

425. State the properties of iodine.

426. What is the nature of Iodide of Sulphur?

427. Give the analytical reaction of iodides.

428. Which three substances may indirectly be detected by a mixture of iodide of potassium and mucilage of starch?

429. Describe a method by which iodides may be removed from a solution containing chlorides and bromides.

HYDROCYANIC ACID AND OTHER CYANIDES.

Formula of Hydrocyanic Acid HCN or HCy.

Molecular weight 27.

History of Cyanogen.—The acidulous radical of hydrocyanic acid and other cyanides is a compound body, cyanogen (Cy). It is so named from κύανος, *kuanos*, blue, and γεννάω, *gennaō*, I generate, in allusion to its prominent chemical character of forming, with iron, the different varieties of Prussian blue. It was from Prussian blue that Scheele, in 1782, first obtained what we now, from our knowledge of its composition, term hydrocyanic acid, but which he called Prussic acid. Cyanogen was isolated by Gay-Lussac in 1814, and was the first compound radical distinctly proved to exist.

Sources.—Cyanogen does not occur in nature, and is only formed from its elements under certain circumstances. It is found in small quantities among the gases of iron-furnaces, and is produced to a slight extent in distilling coals for gas. In the form of ferrocyanide of potassium it is obtained abundantly by heating animal refuse containing nitrogen, such as the scrapings of horns, hoofs, and hides (5 parts), with carbonate of potassium (2 parts) and waste iron (filings, etc.) in a covered iron pot. The residual mass is boiled with water, the mixture filtered, and the filtrate evaporated and set aside for crystals to form. The cyanogen, produced from the carbon and nitrogen of the animal matter, unites with the potassium, and afterwards, on boiling with water, with iron, to form what is known as the yellow prussiate of potash (*Potassæ Prussias Flava*, B. P.), or ferrocyanide of potassium ($K'_4Fe''Cy'_6,3H_2O$) (*Potassii Ferrocyanidum*, U. S. P.), a compound occurring in four-sided tabular yellow crystals. It contains the elements of cyanogen, yet it is not a cyanide, for it is not poisonous, and is otherwise different from cyanides; it will be further noticed subsequently. From this salt all cyanides are directly or indirectly prepared.

Cyanide of potassium (KCy) (*Potassii Cyanidum*, U. S. P.), which is the most common, is procured by fusing 8 parts of ferrocyanide with 3 of carbonate of potassium in a crucible; carbonic acid gas (CO_2) is evolved, iron (Fe) is set free, and cyanate of potassium (KCyO), a body that will be subsequently noticed, is formed at the same time:—

$$2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 2KCyO + Fe_2 + 2CO_2.$$

Double cyanides exist, such as the cyanide of sodium and silver (NaCy,AgCy), formed in the process (subsequently described) of quantitatively determining the amount of hydrocyanic acid in a liquid by a standard solution of nitrate of silver; these compounds have, more or less, the properties of their constituents. But other cyanogen compounds, not double cyanides, occur in which the cyanogen is so intimately united with a metal as to form a distinct radical; such are ferrocyanides and ferridcyanides—salts which will be noticed in due course.

Cyanogen, like chlorine, bromine, and iodine, is univalent (Cy′). It may be isolated by simply heating mercuric cyanide ($HgCy_2$) or cyanide of silver (AgCy). It is a colorless gas, burning, when ignited, with a beautiful peach-blossom-colored flame.

Mercuric cyanide is produced in crystals on dissolving 1 part of ferrocyanide of potassium in 15 parts of boiling water, adding 2 parts of mercuric sulphate, keeping the whole hot for ten or fifteen minutes, and then filtering and setting aside to cool. In addition to mercuric cyanide ($HgCy_2$), mercury (Hg), ferric sulphate (Fe_23SO_4), and sulphate of potassium (K_2SO_4), are formed. Any excess of ferrocyanide also gives Prussian blue by reaction with the ferric sulphate. It (*Hydrargyri Cyanidum*, U. S. P.) may also be made by dissolving red oxide of mercury in diluted hydrocyanic acid. A small flame of cyanogen may be obtained on heating a few crystals of mercuric cyanide in a short piece of glass tubing closed at one end, and applying a light to the other end as soon as evolution of gas commences; brown *paracyanogen* (C_3N_3) and mercury remain.

REACTIONS.

Diluted Hydrocyanic Acid.

Synthetical Reaction.—Dissolve 2 or 3 grains of ferrocyanide of potassium in 5 or 6 times its weight of water in a test-tube, add a few drops of sulphuric acid and boil the mixture, conveying the evolved gas by a bent glass tube (adapted to the test-tube by a cork) into another test-tube containing a little water; the product is a dilute solution of hydrocyanic acid. Made by this process in large quantities of a certain definite strength (2 per cent.), this solution is the *Acidum Hydrocyanicum Dilutum*, U. S. P. "A colorless liquid of a peculiar odor. Specific gravity 0.997."

$$2K_4FeCy_6 + 6H_2SO_4 = FeK_2Fe''Cy_6 + 6KHSO_4 + 6HCy.$$

The following are the details of the official (U. S. P.) process:—

Place 20 parts of Ferrocyanide of Potassium in coarse powder in a tubulated retort, and add to it *forty* (40) *parts* of Water. Connect the neck of the retort (which is to be directed upward), by means of a bent tube, with a well-cooled condenser, the delivery-tube of which terminates in a receiver surrounded with ice-cold water, and containing *sixty* (60) *parts* of Diluted Alcohol. All the joints of the apparatus, except the neck of the receiver, having been made air-tight, pour into the retort, through the tubulure, the Sulphuric Acid previously diluted with an equal weight of Water. Agitate the retort gently, and then heat it, in a sand-bath, until the contents are in brisk ebullition, and continue the heat regularly until there is but little liquid mixed with the saline mass remaining in the retort.* Detach the receiver, and add to its contents so much Distilled Water as may be required to bring the product to the strength of *two* (2) *per cent.* of absolute Hydrocyanic Acid. (*Vide* paragraphs on quantitative analysis.)

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* This operation is peculiarly liable to those sudden and tumultuous evolutions of vapor, or "bumpings," or "*soubresauts*," which often interfere with successful distillation. Such phenomena occur, according to Tomlinson, whenever unaided heat has to overcome the great amount of adhesion naturally existing between certain liquids and vapors, or, rather, between the normal liquid and those particles of it which, be-

The residue of this reaction is acid sulphate of potassium ($KHSO_4$), which remains in solution, and ferrocyanide of potassium and iron ($Fe''K_2FeCy_6$), an insoluble powder sometimes termed Everitt's yellow salt, from the name of the chemist who first made out the nature of the reaction. The latter compound becomes bluish-green during the reaction, owing to absorption of oxygen.

Diluted hydrocyanic acid may also be prepared by reaction of cyanide of silver (6 parts), hydrochloric acid (5 parts), and distilled water (55 parts).——Mix the hydrochloric acid with the distilled water, add the cyanide of silver, and shake the whole together in a glass-stoppered bottle. When the precipitate has subsided, pour off the clear liquid.

Pure anhydrous hydrocyanic acid is a colorless, highly volatile, intensely poisonous liquid, solidifying when cooled to a low temperature.* It may be made by passing sulphuretted hydrogen over mercuric cyanide. The official solution of the acid is fairly stable, but is said to be rendered more so by the presence of a minute trace of sulphuric or hydrochloric acid. A stronger acid is liable to assimilate the elements of water, and yield formiate of ammonium (NH_4CHO_2). Solutions of hydrocyanic acid often become brown by formation of what is, apparently, *paracyanogen* (C_3N_3). According to Williams, aqueous hydrocyanic acid containing 20 per cent. of glycerin can

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coming strongly heated at the heated part of the vessel, have assumed the condition of particles of dissolved vapor, and which would at once pass from this condition into that of permanent vapor but for adhesion. Ordinarily a glass or other surface is not absolutely clean, but is more or less covered with specks, traces of materials deposited from the air, the fingers, cloths, etc. Some liquids seem to have little or no adhesion for these materials, while certain vapors have greater adhesion for the films than for the liquids. Hence, in ordinary regular ebullitions the vapors accumulate on the films, and then at once become subject to the pressure of the mass of fluid, and so pass off in bubbles. But when the films are absent, or have become removed during distillation, the heat accumulates until it is sufficient to overcome the adhesion of the superheated particles, and these are then, all of them at once, converted into vapor, the liquid commonly boiling over, sometimes even bursting the vessel. "Bumping" would be prevented by the introduction of fragments of substances for which vapor-particles have adhesion, but no known substance has this property in an absolute degree. Fragments of tobacco-pipe or pumice-stone, pieces of cork, thick paper, resin, sulphur, platinum wire, etc., are all useful when there is no chemical action between them and the liquid. Mr. Tomlinson very strongly recommends cocoanut-shell charcoal to be used whenever practicable. A slow current of gas, such as hydrogen, air, or carbonic acid gas, also usefully promotes escape of vapor from a liquid. A jet of steam prevents bumping, but is not always applicable. When the bumping cannot well be prevented, as in the distillation of sulphuric acid, it is somewhat reduced in violence if the retort be heated by an annular gas-burner rather than by a single central jet.

* Traces are formed when electricity passes between carbon poles in slightly moist air (Dewar).

be kept for an apparently indefinite length of time. The official acid should be preserved in small stoppered bottles in a cool dark place.

Note.—A few drops of diluted hydrocyanic acid so placed that its vapor may be inhaled, forms the *Vapor Acid Hydrocyanici*, B. P., or Inhalation of Hydrocyanic Acid.

Hydrocyanic acid also occurs in cherry-laurel water and bitter-almond water (*vide* Index).

The hydrocyanic acid used in pharmacy is extremely liable to variation in strength. It should frequently be tested volumetrically.

Analytical Reactions (*Tests*).

First Analytical Reaction.—To a few drops of the hydrocyanic acid solution produced in the above reaction, or to any solution of a cyanide, add excess of solution of nitrate of silver; a white precipitate of cyanide of silver (AgCy) falls. When the precipitate has subsided, pour away the supernatant liquid, and place half of the residue in another test-tube: to one portion add nitric acid, and notice that the precipitate does not dissolve; to the other add ammonia, and observe that the precipitate is insoluble or only sparingly soluble. (Chloride of silver, which is also white, is readily soluble in ammonia.) Cyanide of silver dissolves in solutions of cyanides of alkali-metals, soluble double cyanides being formed (*e. g.*, KCy,-AgCy).

Solubility of precipitates in strong solutions of salts.—Cyanide of silver and many other precipitates insoluble in acids (similar remarks apply to precipitates insoluble in alkalies) are often soluble in the strong saline liquids formed by the addition of acids and alkalies to one another. Hence the precaution of adding the latter reagents to separate portions of a precipitate, or of not adding the one until the other has been poured away.

Cyanogen in an insoluble cyanide, such as cyanide of silver itself, is readily recognized on heating the substance in a short piece of glass tubing closed at one end like a test-tube and drawn out at the other end, so as to have but a small opening; on applying a flame, the escaping cyanogen ignites and burns with a characteristic peach-blossom tint. Metallic silver remains.

Antidote.

Second Analytical Reaction.—To a dilute solution of hydrocyanic acid, or a soluble cyanide, add a few drops of solution of a ferrous salt and a drop or two of solution of a ferric salt (ferrous sulphate and ferric chloride are usually at hand); to the mixture add potash or soda (magnesia or carbonate of sodium), and then hydrochloric acid; a precipitate of Prussian blue remains. The decompositions may be traced in the following equations:—

$$
\begin{array}{llllll}
HCy & + KHO & = KCy & + H_2O \\
2KCy & + FeSO_4 & = FeCy & + K_2SO_4 \\
4KCy & + FeCy_2 & = K_4FeCy_6 & \text{or } K_4Fcy \\
3K_4Fcy & + 2Fe_2Cl_6 & = 12KCl & + Fe_4Fcy_3.
\end{array}
$$

The test depends on the conversion of the cyanogen into ferrocyanogen by aid of the iron of a ferrous salt, and the combination of the ferrocyanogen, so produced, with the iron of a ferric salt.

Hence a mixture of green sulphate of iron, solution of perchloride of iron, and either magnesia or carbonate of sodium, is the recognized *antidote* in cases of poisoning by hydrocyanic acid or cyanide of potassium.

In such an alkaline mixture the poisonous cyanide, by reaction with ferrous hydrate, is at once converted into innocuous ferrocyanide of potassium or sodium, etc.; should the mixture become acid, the ferric salt present reacts with the soluble ferrocyanide, forming insoluble Prussian blue, which is also inert. From the rapidity of the action of these poisons, however, there is seldom time to prepare an antidote. Emetics, the stomach-pump, the application of a stream of cold water to the spine, and the above antidote, form the usual treatment.

Third Analytical Reaction.—To solution of hydrocyanic acid add ammonia and common yellow sulphydrate of ammonium, and evaporate the liquid nearly or quite to dryness in a small dish, occasionally adding ammonia till the excess of sulphydrate of ammonium is decomposed; add water and acidify the liquid with hydrochloric acid, and then add a drop of solution of a ferric salt; a blood-red solution of sulphocyanide of iron will be formed.

This is a very delicate reaction. Some free sulphur in the yellow sulphydrate of ammonium unites with the alkaline cyanide and forms sulphocyanate ($2AmCy + S_2 = 2AmCyS$); the ammonia combines with excess of free sulphur, and forms, among other salts, sulphydrate of ammonium, the whole of which is removed by the ebullition. If the liquid has not been evaporated far enough, sulphydrate of ammonium may still be present, and give black sulphide of iron on the addition of ferric salt.

Hydrocyanic Acid in the Blood.—According to Buchner the blood of animals poisoned by hydrocyanic acid, instead of coagulating as usual, remains liquid and of a clear cherry-red color several days. In one case he obtained the reactions of the acid on diluting and distilling the blood fifteen days after death, and applying the usual reagents to the distillate. Aqueous solution of peroxide of hydrogen (p. 102) changes such blood to a deep-brown color.

Schönbein's test for hydrocyanic acid is said to be extremely delicate. Filtering-paper is soaked in a solution of 3 parts of guaiacum resin in 100 of alcohol. A strip of this paper is dipped in a solution of 1 part of sulphate of copper in 50 of water; a little of the suspected solution is placed on this paper and exposed to the air, when it immediately turns blue. Or the paper may be placed over the neck of an open bottle of medicine supposed to contain hydrocyanic acid, or otherwise exposed to the vapor of the acid.

QUESTIONS AND EXERCISES.

430. Write a paragraph on the history of cyanogen.

431. Mention the source of the cyanogen of cyanides.

432. How is Ferrocyanide of Potassium prepared?

433. What is the formula of ferrocyanide of potassium?

434. Is ferrocyanide of potassium poisonous?

435. Write an equation expressive of the reaction which ensues when ferrocyanide and carbonate of potassium are brought together at a high temperature.

436. What are the properties of cyanogen? How may it be obtained in a pure condition?

437. How is mercuric cyanide prepared?

438. How much real hydrocyanic acid is contained in the official liquid?

439. Give details of the preparation of hydrocyanic acid, and an equation of the reaction.

440. State the proportion of water that must be added to an aqueous solution containing 15 per cent. of hydrocyanic acid to reduce the strength to 2 per cent.—*Ans.* 6½ to 1.

441. What are the characters of pure undiluted hydrocyanic acid? How may it be obtained?

442. Enumerate the tests for cyanogen, giving equations.

443. Explain the action of the best antidote in cases of poisoning by hydrocyanic acid or cyanide of potassium.

NITRIC ACID AND OTHER NITRATES.

Formula of Nitric Acid HNO_3. Molecular weight 63.

Introduction.—The group of elements represented by the formula NO_3 is that characteristic of nitric acid and all other nitrates; hence it is expedient to regard these elements as forming an acidulous radical, which may be termed *the nitric radical.* Like the hypothetical basylous radical ammonium (NH_4), this supposed acidulous radical (NO_3) has not been isolated. Possibly it is liberated when chlorine is brought into contact with nitrate of silver; but, if so, its decomposition into white crystalline nitric anhydride (N_2O_5) and oxygen (O) is too rapid to admit of its identification.

Sources.—The nitrogen and oxygen of the air combine and ultimately form nitric acid whenever a current of electricity (as in the occurrence of lightning) passes. The nitrates found in rain may partly or wholly thus originate. The oxidation of ammoniacal matter and of the nitrogenous constituents of animal and vegetable matter in the soil, favored by the darkness and, probably, by the presence of some low form of vegetable life acting as a ferment, result in the production of nitrates. Hence nitrates are commonly met with in waters, soils, and the juices of plants. In the concentrated plant-juices termed medicinal "Extracts," small prismatic crystals of nitrate of potassium may occasionally be observed. (The cubical crystals often met with on extracts are chloride of potassium.) Nitric acid and other nitrates are obtained from nitrates of potassium and sodium, and these form the surface layers of the soil of tropical countries. *Nitrate of potassium* or *prismatic nitre* (from the form of its crystals) is chiefly produced in and about the villages of India. The natives simply scrape the surface of waste grounds, mud-heaps, banks, and other spots where a slight incrustation indicates the presence of appreciable quantities of nitre, mix the scrapings with wood ashes (carbonate of potassium, to decompose the nitrate of calcium always present), digest the mixture in water, and evaporate the liquor. The impure product is purified by careful recrystallizations, and is sent into commerce in the form of white crystalline masses or fragments of striated six-sided prisms. Besides its use in medicine (*Potassii Nitras*, U. S. P.), it is employed in very large quantities in the manufacture of gunpowder. *Charta Potassii Nitratis*, U. S. P., Nitrate-of-Potassium Paper, is made by immersing strips of white unsized paper in a solution of 1 part of the salt in 4 parts of water and drying them. *Nitrate of Sodium* (*Sodii Nitras*, U. S. P.) occurs in deposits from 3 inches to 3 yards in thickness on and near the surface, and at any depth down to about 30 feet, in many parts of Peru, Bolivia, and Chili, but more especially in the district of Atacama. The mineral is termed *caliche*, and commonly contains 50 per cent. of nitrate of sodium. The latter is distinguished as Chili saltpetre or (from the form of its crystals—obtuse rhomboids) cubic nitre, and is chiefly used as a manure and as a source of nitric acid, its tendency to absorb moisture unfitting it for use in gunpowder. In many parts of Europe nitrate of potassium is made artificially by exposing heaps of animal manure, refuse, ashes, and soil to the action of the air and the heat of the sun: in the course of a year or two the nitrogen of the animal matter becomes oxidized to nitrates; the latter are removed by washing. According to Warington, the nitrifying ferment appears capable of existing in three conditions:—1, the nitric ferment of soil, which converts both ammonium salts and nitrites into nitrates; 2, the altered ferment, which converts ammonium salts into nitrites, but fails to change nitrites into nitrates; and, 3, the surface organism (a bacterium) which changes nitrites into nitrates.

Note.—The word *nitric* is from *nitre*, the English equivalent of the Greek *νίτρον* (nitron), a name applied to certain natural deposits of *natron* (carbonate of sodium), for which nitrate of potassium seems at first to have been mistaken. *Saltpetre* is simply *sal petræ*, salt of the rock, in allusion to the natural origin of nitrate of potassium. *Sal prunella* (from *sal*, a salt, and *pruna*, a live coal) is nitrate of potassium melted over a fire and cast into cakes or bullets.

The nitric radical is univalent (NO_3').

Constitution of Salts.

It is here necessary again to caution the reader against regarding salts as invariably possessing a known constitution, or supposing that they always possess two or more sides or contain definite radicals. The erroneous conception which, of all others, is most likely to be imperceptibly formed is that of considering salts to be binary bodies. For, first, the names of salts are necessarily binary. A student hears the names "sulphate of iron," "sulphate of copper," and simultaneously receives the impression that each salt has two sides, copper or iron occupying one, and something indicated by the words "sulphate of" the other. Such words as "vitriol," green or blue, or "nitre," would perhaps implant unitary ideas in the mind; but it is simply impossible to give such names to all salts as will convey the impression that each salt is a whole, and therefore unitary. The name "sulphate of potash" produces binary impressions; and the less incorrect name, "sulphate of potassium," is in this respect no better. Secondly, it is impracticable to study salts as a whole. Teachers are almost unanimous in the opinion that students should first master the reactions characteristic of the metals in salts, and then the residues which, with those metals, make up the salts, or *vice versâ*. It is not only impracticable, but impossible, to study salts as a whole; binary ideas concerning them are therefore almost inevitably imbibed. We come to regard a salt as a body which splits up in one direction only, look upon nitre, for instance, and all other nitrates, as containing NO_3 and a metal K; whereas KNO_3 may be split up into KNO_2 and O; or into K_2O, N_2, and O_5; or may contain K_2O and N_2O_5. These are the chief disadvantages attending the employment of the binary hypothesis in studying chemical compounds; if they be borne in mind, the hypothesis may be freely used without much danger of permanent mental bias. Thus in nitre let the group of elements (NO_3) which, with potassium, makes up the whole salt be called the nitric radical, the name of the latter being directly derived from its hydrogen salt. Similarly allow the acidulous residues of other salts of metals to be termed respectively the chloric, acetic, sulphurous, sulphuric, carbonic, oxalic, tartaric, phosphoric, citric, boracic radicals. In short, these compound radicals should be regarded as groupings common to many salts, and which may usually be transferred without any apparent breaking or splitting; at the same time we must be prepared to find that occasionally a salt divides in other directions. In this way perhaps erroneous impressions will gain least hold on the mind, and a way be left open for the easy entrance of new truths should the real constitution of salts be discovered.

Formerly salts (such as sulphate of magnesium) were regarded as containing (*a*) an oxide of a metal (MgO) and an anhydride (SO_3), the latter being incorrectly called an acid (sulphuric acid); or (*b*) as containing two simple radicals (*e. g.*, KI, NaCl, KCy, HgS)—the former being called *oxyacid salts*, or *oxysalts*, and the latter *haloid salts* (from *αλς*, *als*, sea-salt, and *ειδος*, *eidos*, likeness). Such distinction is no longer maintained, the two classes being merged. This is an important educational gain on the side of simplicity; for, whereas under the old system much time was necessarily expended before salts of a metal and salts of the oxide of that metal could be distinguished (*e. g.*, KI and K_2O,SO_3), now, all salts being regarded as salts of the metals themselves (*e. g.*, KI and K_2SO_4), no such distinction is necessary.

REACTIONS.

Nitric Acid.

Synthetical Reaction.—To a fragment of nitrate of potassium or nitrate of sodium in a test-tube add a drop or two of sulphuric acid, and warm; nitric acid (HNO_3) is evolved in vapor. The fumes may be condensed by a bent tube fitted to the test-tube, not by a cork as for hydrochloric acid—because the nitric vapors would strongly act on it—but by plaster of Paris, a paste of which sets hard on being set aside for a short time, and is unaffected by the acid.

On a somewhat larger scale nitric acid may be prepared by heating, in a stoppered or plain retort, a mixture of equal weights of nitrate of potassium and sulphuric acid; the acid distils over, and acid sulphate of potassium remains behind:—

$$\underset{\text{Nitrate of potassium.}}{KNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Acid sulphate of potassium.}}{KHSO_4}$$

Half the quantity of sulphuric acid may be taken; but in that case neutral sulphate of potassium (K_2SO_4) is produced, which, from its hard, slightly soluble character, is removed with difficulty from the retort. On the manufacturing scale the less proportion is used; but instead of retorts iron cylinders are employed, from which the residual salt is removed by chisels. Moreover, the cheaper sodium salt is the nitrate, from which manufacturers usually prepare nitric acid, seven parts of nitrate of sodium and four of sulphuric acid being employed.

Note.—The acid sulphate of potassium is readily converted into neutral sulphate (*Potassii Sulphas*, U. S. P.) by dissolving in water, adding carbonate of potassium until effervescence ceases to occur, filtering, and setting aside to crystallize.

Pure nitric acid (HNO_3) is a colorless liquid, somewhat difficult of preparation; its specific gravity is 1.52. The strongest acid met with in commerce has a sp. gr. of 1.5, and contains 93 per cent. of real nitric acid (HNO_3); it fumes disagreeably, is unstable, and, except as an escharotic, is seldom used. The United States Pharmacopœia contains two acids: *Acidum Nitricum*, of sp. gr. 1.42, and containing 69.4 per cent. of real acid (HNO_3); and another, *Acidum Nitricum Dilutum*, sp. gr. 1.059, containing 10 per cent.

The stronger liquid, although containing water, is usually simply termed "nitric acid." The official nitric acid, of sp. gr. 1.42, is a definite hydrous acid ($2HNO_3,3H_2O$); it distils at 250° F. without change. If a weaker acid be heated it loses water; if a stronger acid be heated it loses nitric acid, until the density of 1.42 is reached. *Aqua fortis* is an old name for nitric acid (*Aqua fortis simplex*, sp. gr. 1.22 to 1.25; *Aqua fortis duplex*, 1.36). The strength of a specimen of nitric acid is determined by volumetric analysis. *Nitric anhydride* (N_2O_5), sometimes but erroneously called *anhydrous nitric acid*, is a solid crystalline substance formed on passing dry chlorine over dry nitrate of silver. Metals reduce nitric acid to nitrous acid and to the various oxides of nitrogen, or even to nitrogen itself, according to the strength of acid, temperature, and amount of nitrate present. Not unfrequently nitrate of ammonium is simultaneously formed. Thus, with zinc:—

$$10HNO_3 + 2Zn_2 = 4(Zn2NO_3) + NH_4NO_3 + 3H_2O.$$

Aqua Regia.—Four parts of nitric acid and fifteen of hydrochloric acid by weight form the *Acidum Nitrohydrochloricum*, U. S. P., and the same weights with 76 of water, give the *Acidum Nitrohydrochloricum Dilutum.*

$$\underset{\text{Nitric acid.}}{2HNO_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl} = \underset{\substack{\text{Chloronitric}\\ \text{gas.}}}{N_2O_2Cl_4?} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Chlorine.}}{Cl_2}$$

In the later stages of the reaction, the decomposition expressed in the following equation also probably occurs:—

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{3HCl} = \underset{\substack{\text{Chloronitrous}\\ \text{gas.}}}{NOCl} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}$$

The same reaction occurs if the acids are mixed after dilution, but is not complete for a week or a fortnight (Tilden). The undiluted mixture of acids is known as *aqua regia*, so called from its property of dissolving gold, "the king" of metals.

This "diluted nitrohydrochloric acid" is quite strong enough to attack organic matter, with evolution of nitrous gases, hence should not be dispensed with tinctures, etc., in too concentrated a form.

Analytical Reactions (Tests).

First Analytical Reaction.—To a solution of any nitrate (*e. g.*, KNO_3) add sulphuric acid, and then copper turnings, and warm; colorless nitric oxide gas (NO) is evolved, which at once unites with the oxygen in the tube, giving *red fumes* of nitric peroxide or peroxide of nitrogen (NO_2).

$$2KNO_3 + 5H_2SO_4 + Cu_3 = 2NO + 3CuSO_4 + 4H_2O + 2KHSO_4;$$
$$\text{then,}\quad 2NO + O_2 = 2NO_2.$$

Performed on a larger scale, in a vessel to which a delivery-tube is attached, the reaction of nitric acid on copper becomes of synthetical interest, being the process for the preparation of nitric oxide gas for the purposes of chemical experiment.

Small amounts of a nitrate may be overlooked by this test, the color of the red fumes not being very intense.

Undiluted nitric acid poured on to copper turnings gives dense red vapors of *nitrous acid* (HNO_2), *nitrous anhydride* (N_2O_3), *nitric peroxide* (NO_2), *nitric oxide* (NO), and even *nitrogen* (N_2), the reaction varying somewhat according to the temperature of the mixture and (Ackworth) the amount of nitrate of copper in solution. Diluted nitric acid gives nitric oxide, $Cu_3 + 8HNO_3 = 3(Cu2NO + 4H_2O + 2NO$.

Second Analytical Reaction.—To a cold solution of the nitrate, even if very dilute, add three or four crystals of sulphate of iron, shake gently for a minute in order that some of the sulphate may become dissolved, and then pour eight or ten drops of strong sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom of the vessel; a reddish-purple or black coloration will appear between the acid and the supernatant liquid.

This is a very delicate test for the presence of nitrates. The black color is due to a solution or, perhaps, combination of nitric oxide with a portion of the ferrous salt. The nitric oxide is liberated from the nitrate by the reducing action of the hydrogen of the sulphuric acid, the sulphuric radical of which is absorbed by the ferrous sulphate, the latter salt becoming ferric sulphate.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 4H_2O + 3(Fe_23SO_4) + 2NO.$$

The process of oxidation is one frequently employed in experimental chemistry; and nitrates, from their richness in oxygen, but more especially because always at hand, are the oxidizers usually selected for the purpose. In the operation they generally split up in one way, namely, into oxide of their basylous radical, nitric oxide gas, and available oxygen. Thus hydrogen nitrate (nitric acid) yields oxide of hydrogen (water) and the other bodies mentioned, as shown in the following equation:—

$$4HNO_3 = 2H_2O + 4NO + 3O_2.$$

When nitrates, other than nitric acid, are used for the purpose of oxidation, a stronger acid, generally sulphuric, is commonly added in order that nitric acid may be formed; the hydrogen nitrate splitting up more readily than other nitrates.

The five oxides of nitrogen have now been mentioned, namely—

Nitrous oxide	N_2O	or	N_2O
Nitric oxide*	NO		N_2O_2
Nitrous anhydride . .	N_2O_3		N_2O_3
Nitric peroxide* . . .	NO_2		N_2O_4
Nitric anhydride . . .	N_2O_5		N_2O_5

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* The specific gravities of these gases indicate that NO and NO_2 are the correct formulæ, and not N_2O_2 and N_2O_4.

Nitrous oxide is a colorless gas not altered by exposure to air; nitric oxide is also colorless, but gives red fumes in the air; nitrous anhydride is a red vapor condensible to a blue liquid; nitric peroxide is a red vapor condensible to an orange liquid; nitric anhydride is a colorless crystalline solid. The two anhydrides by absorbing water yield respectively nitrous acid (HNO_2) and nitric acid (HNO_3). Nitrous oxide is also probably an anhydride, the acid of which would doubtless have the formula HNO, while the silver and sodium salts certainly have the formulæ $AgNO$ and $NaNO,3H_2O$ (Divers; Menke). The above series of compounds forms a good illustration of the doctrine of multiple proportions (p. 50).

Third Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red hot; now place on the spot a fragment of nitrate; deflagration ensues.

This reaction does not distinguish nitrates from chlorates. It is insufficient for the recognition of very small quantities of either class of salts, especially when they are mixed with other substances.

Gunpowder is an intimate mechanical mixture of 75 parts of nitre, 15 to 12½ parts of charcoal, and 10 to 12½ parts of sulphur. In burning it may be said to give sulphide of potassium (the white smoke), (K_2S), nitrogen (N), carbonic oxide (CO), and carbonic acid (CO_2) gases, though the decomposition is seldom complete. The sudden production of a large quantity of heated gas from a small quantity of a cold solid is sufficient to account for all the effects of gunpowder.

Fourth Analytical Reaction.—To nitric acid or other nitrate add solution of "sulphate of indigo;" the color is discharged.

Test-Solution of Indigo. U. S. P. (Sulphindylic or Sulphindigotic acid), is made by digesting 1 part of dry, finely powdered indigo in 12 parts of strong sulphuric acid in a test-tube for an hour, the mixture being kept hot by a water-bath; the blue liquid is then poured into 500 parts of sulphuric acid, the whole well shaken, set aside, and the clear liquid decanted. Free chlorine also destroys the color of this reagent.

Indigo, U. S. P. (C_8H_5NO), is a blue coloring-matter deposited when infusion of various species of *Indigofera* is exposed to air and slight warmth. Under these circumstances *indican*, a yellow transparent amorphous substance, soluble in water, breaks up into indigo, which is insoluble and falls as a sediment, and a sort of sugar termed *indiglucin*. The indigo is collected, drained, pressed, and dried. By action of deoxidizing agents indigo is converted into soluble colorless *indigogen*, *reduced indigo* or *white indigo* (C_8H_6NO); 1 part of powdered indigo, 2 of green sulphate of iron, 3 of slaked lime, and 200 of water, shaken together and set aside in a well-closed bottle, give this colorless indigo. A piece of yarn, calico, or similar fabric dipped into such a solution, and exposed to air, becomes dyed blue, deposition of insoluble indigo-blue occurring within the cells and vessels of the fibre. This operation is readily performed on the small scale, and forms a good illustration of the characteristic feature of the art of dyeing, namely, the introduction of soluble coloring-matter into a fabric by permeation of the walls of its cellular and vascular tissue, and the imprisonment of that coloring-matter by conversion into a solid and insoluble form (*vide* also p. 137).

Pure indigo, or *indigotin*, may be obtained in beautiful needles by spreading a paste of indigo and plaster of Paris on a tin plate, and when dry placing a lamp underneath, moving the latter from place to place as the indigo sublimes and condenses on the surface of the plaster. It may also be obtained in crystals by gently boiling finely powdered indigo with aniline, filtering while hot, and setting aside; these crystals may be washed with alcohol. Hot paraffin may be employed instead of aniline. It is possible to obtain indigotin artificially; indeed Baeyer relates that indigo can be made economically from benzol, this being first converted into isatine chloride.

Distinction between Nitric Acid and other Nitrates.—Presence of the nitric radical in a solution having been proved by the above reactions, its occurrence as the nitrate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper and the detection of the metal, its occurrence as nitric acid by the sourness of the liquor to the taste and the effervescence produced on the addition of a carbonate.

Antidote.—In cases of poisoning by strong nitric acid, solution of carbonate of sodium (common washing soda) or a mixture of magnesia and water may be administered as antidotes.

QUESTIONS AND EXERCISES.

444. Trace the origin of nitrates.

445. In what does cubic nitre differ, chemically, from prismatic nitre?

446. Describe a process by which nitrate of potassium may be obtained artificially.

447. State the difference between nitrate of potassium, nitre, saltpetre, and sal prunella.

448. What group of elements is characteristic of all nitrates? and what claim has this group to the title of radical?

449. Mention the usual theory regarding the manner in which atoms are arranged with reference to each other in such salts as nitrate of potassium.

450. How is Nitric Acid prepared?

451. Give the properties of nitric acid.

452. What reactions occur when strong nitric and hydrochloric acids are mixed?

453. How is nitric oxide prepared?

454. Enumerate and explain the tests for nitrates.

455. Into what substances does nitric acid usually split when employed as an oxidizing agent?

456. How is nitrous oxide prepared?

457. Enumerate the five oxides of nitrogen.

458. What is the nature of gunpowder?

459. Write a few sentences on the chemistry of indigo, one of the tests for nitric acid.

460. How is nitric acid distinguished from other nitrates?

461. What quantity of cubic nitre will be required to produce ten carboys of official nitric acid, each containing 114 pounds?—*Ans.* 1076⅔ pounds.

CHLORIC ACID AND OTHER CHLORATES.

Formula of Chloric Acid $HClO_3$. Molecular weight 84.4.
Chlorates are made from hypochlorites.

Hypochlorous Acid ($HClO$) and other Hypochlorites.

Place a few grains of red oxide of mercury in a test-tube, half fill the tube with chlorine-water, and well shake the mixture; the resulting liquid is a solution of hypochlorous acid, mercuric oxychloride remaining undissolved:

$$2HgO + 2Cl_2 + H_2O = HClO + Hg_2OCl_2.$$

By the metathesis (double decomposition) of hypochlorous acid and oxides or hydrates, other pure hypochlorites are formed:—

$$HClO + NaHO = NaClO + H_2O.$$

The direct action of chlorine on metallic hydrates and some carbonates is supposed to give a mixture of chloride and hypochlorite, as described in connection with the synthetical reactions of Calcium (p. 111, *Calx Chlorata*, U. S. P.)

$$Cl_2 + 2NaHO = NaCl,NaClO + H_2O;$$
$$2Cl_2 + 2CaH_2O_2 = CaCl_2,Ca2ClO + 2H_2O.$$

The condition of chlorides in these bodies is not satisfactorily made out; so that their constitution is not definitely determined. The action of acids on them results in the evolution of chlorine; hence the great value of the calcium compound (chlorinated lime, or chloride of lime) in bleaching operations:—

$$CaCl_2,Ca2ClO + 2H_2SO_4 = 2Cl_2 + 2CaSO_4 + 2H_2O.$$

The solubility of hypochlorites in water, their peculiar odor, greatly intensified on the addition of acid, and their bleaching powers (see the above Calcium reaction) are the characters on which to rely in searching for hypochlorites.

Chlorates.

The group of elementary atoms represented by the formula ClO_3 is that characteristic of chloric acid and all other chlorates; hence it is expedient to regard it as being an acidulous radical, which may be termed the chloric radical. Like the nitric radical, it has not been isolated. Chloric anhydride (Cl_2O_5), unlike nitric anhydride, has not yet been obtained in the free condition.

Chlorates are artificial salts. They are formed by simply boiling aqueous solution of the common bleaching salts (chlorinated lime, chlorinated soda, chlorinated potash). Heat thus converts

$3(NaCl, NaClO)$ Chlorinated soda.	into	$NaClO_3$ Chlorate of sodium.	and	$5NaCl$ Chloride of sodium.
$3(KCl, KClO)$ Chlorinated potash.	into	$KClO_3$ Chlorate of potassium.	and	$5KCl$ Chloride of potassium.
$3(CaCl_2, Ca2ClO)$ Chlorinated lime.	into	$Ca2ClO_3$ Chlorate of calcium.	and	$5CaCl_2$ Chloride of calcium.

One chlorate may also be made from another by double decomposition. In making chlorates economically the chlorinated salt is, of course, at once converted into chlorate.

Chlorate of Potassium.

Thus Chlorate of Potassium (*Potassii Chloras*, U. S. P.) is commercially made by saturating with chlorine gas a moistened mixture of three parts of chloride of potassium and ten of slaked lime, and well boiling the product. Chlorinated lime is first formed; this, on continued boiling with water, splits up into chloride of calcium and chlorate of calcium, and the latter, reacting on the chloride of potassium, yields chloride of calcium and chlorate of potassium.

$$6(Ca2HO) + 6Cl_2 = 3(CaCl_2,Ca2ClO) + 6H_2O;$$
$$3(CaCl_2,Ca2ClO) = Ca2ClO_3 + 5CaCl_2;$$
$$Ca2ClO_3 + 2KCl = CaCl_2 + 2KClO_3.$$

This operation may be conducted on a small scale by rubbing together in a mortar the above proportions of ingredients in ounces or half ounces, adding enough water to make the whole assume the character of damp lumps, placing the porous mass in a funnel (loosely plugged with stones or pieces of glass), and passing chlorine gas (p. 27) through the mass by attaching the tube delivering the gas to the neck of the funnel. When the whole mass has become of a slight pink tint (due to a trace of permanganate), it should be turned into a dish, *well* boiled with water, filtered, the filtrate evaporated if necessary, and set aside; the chlorate of potassium crystallizes out in colorless rhomboidal plates, chloride of calcium remaining in the mother-liquor.

In the official process carbonate of potassium, instead of chloride, is used; but otherwise it is similar to the method just described. Chlorinated potash and chlorinated lime are first formed :—

$$K_2CO_3 + Ca2HO + Cl_2 = KCl,KClO + CaCO_3 + H_2O,$$
$$6(Ca2HO) + 6Cl_2 = 3(CaCl_2,Ca2ClO) + 6H_2O\,;$$

these, on boiling with water, split up into chlorates and chlorides—

$$3(KCl,KClO) \quad = KClO_3 + 5KCl,$$
$$3(CaCl_2,Ca2ClO) = Ca2ClO_3 + 5CaCl_2\,;$$

the whole of the chloride of potassium and chlorate of calcium finally yielding chlorate of potassium and chloride of calcium—

$$2KCl + Ca2ClO_3 = CaCl_2 + 2KClO_3.$$

Neglecting intermediate decomposition, the reactions may be represented by the following equation :

$$\underset{\text{Chlorine.}}{6Cl_2} + \underset{\substack{\text{Carbonate of}\\\text{potassium.}}}{K_2CO_3} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{6CaH_2O_2} = \underset{\substack{\text{Chlorate of}\\\text{potassium.}}}{2KClO_3} + \underset{\substack{\text{Carbonate of}\\\text{calcium.}}}{CaCO_3}$$
$$+ \underset{\substack{\text{Chloride of}\\\text{calcium.}}}{5CaCl_2} + \underset{\text{Water.}}{6H_2O}$$

Chlorate of Sodium (*Sodii Chloras*, U.S.P.), $NaClO_3$, is similarly prepared.

Chlorate of potassium is soluble in water to the extent of 6 or 7 parts in 100 at common temperatures. It must on no account be rubbed with sulphur in a mortar or otherwise, friction of such a mixture resulting in violent explosion.

Chlorate of potassium, when heated, yields chloride of potassium and oxygen, and is the salt commonly employed in the preparation of the gas for experimental purposes. But if the action be arrested when one-third of the oxygen has escaped, the residual salt is found to contain perchlorate of potassium ($KClO_4$) :—

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Perchloric Acid ($HClO_4$).—Crude perchlorate of potassium, obtained as just indicated, is boiled (in a fume-cupboard) with hydrochloric acid to decompose any chlorate that may be remaining, and then separated from chloride by washing and crystallization, chloride being far more soluble in water than the perchlorate. Perchloric acid is then obtained by distilling the perchlorate of potassium with sulphuric acid; it is quite stable, and is occasionally administered in medicine.

Chloric Acid ($HClO_3$) may be isolated, but is unstable, quickly decomposing into chlorine, oxygen, and perchloric acid; some other chlorate (*e. g.*, $KClO_3$) must therefore be used in studying the reactions of the chloric radical.

Table of the Chlorine Acids.

Hydrochloric acid	HCl.
Hypochlorous acid	$HClO$.
Chlorous acid	$HClO_2$.
Chloric acid	$HClO_3$.
Perchloric acid	$HClO_4$.

The chloric radical is univalent (ClO_3). The acidulous radicals of the other chlorine acids are also univalent, as indicated in the foregoing formulæ.

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of a chlorate (*e. g.*, chlorate of potassium) add solution of nitrate of silver; no precipitate falls, showing that the chlorine must be performing different functions from those it possesses in chlorides. Evaporate the solution to dryness, and place the residue in a small dry test-tube, or at once drop a fragment of a chlorate into a test-tube, and heat strongly; oxygen is evolved, and may be recognized by its power of re-inflaming an incandescent match inserted in the tube. Boil the residue with water, and again add solution of nitrate of silver; a white precipitate falls, having all the characters of chloride of silver, as described under Hydrochloric Acid.

This is a trustworthy test, and, even omitting the recognition of the oxygen, may be applied in the detection of small quantities of chlorates.

Second Analytical Reaction.—To a fragment of a chlorate add two or three drops of strong sulphuric acid; an explosive gas (Cl_2O_4) is evolved, somewhat resembling chlorine in odor, but possessing a deeper color than that element.

$$3KClO_3 + H_2SO_4 = Cl_2O_4 + KClO_4 + K_2SO_4 + H_2O.$$

Warm the upper part of the test-tube to 150° or 200° F., or introduce a hot wire; a sharp explosion ensues, due to decomposition of the gas, peroxide of chlorine, into its elements.

Third Analytical Reaction.—Heat a small fragment of a chlorate with hydrochloric acid: a yellowish-green explosive gas termed *euchlorine* is evolved. Its color is deeper than that of chlorine, hence the name (from εὖ, *eu*, well, and χλωρός, *chlōros*, green). In odor it resembles chlorine, and is probably a mixture of that element with one of the oxides of chlorine.

Fourth Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red hot, and then place on the spot a fragment of a chlorate; deflagration ensues as with nitrates.

Bromates.

Bromates are salts closely resembling chlorates and iodates. The formula of Bromic Acid is $HBrO_3$.

Iodates.

Iodic Acid (HIO_3).—Iodine is boiled in a flask with five times its weight of the strongest nitric acid (sp. gr. 1.5), in a fume-cupboard, until all action ceases. On cooling, iodic acid separates in small pyramidal crystals. These are removed, the residual liquid evaporated to dryness to remove excess of nitric acid, the residue and the first crop dissolved in a small quantity of boiling water, and the solution set aside to crystallize.

Iodate of Potassium (KIO_3).—Powder together equal weights of iodine and chlorate of potassium; to the mixture add twice its weight of water and about one-eighth of its weight of nitric acid; warm the whole until iodine disappears, and evaporate quite to dryness over a water-bath. The residue dissolved in water forms "Solution of Iodate of Potash," B. P. It contains a little nitrate of potassium. In this reaction the small quantity of nitric acid furnishes corresponding amounts of nitrate of potassium and chloric acid. The chloric acid with iodine gives iodic acid and chlorine, thus:—

$$2HClO_3 + I_2 = 2HIO_3 + Cl_2.$$

The iodic acid and some chlorate of potassium then yield chloric acid and iodate of potassium—

$$HIO_3 + KClO_3 = HClO_3 + KIO_3;$$

and the two reactions alternate until the whole of the iodine has displaced the whole of the chlorine.

Iodate of potassium and sulphurous acid decompose each other with elimination of iodine (or with formation of a blue color, if starch be present.) Sulphurous acid occurring as an impurity in acetic and other acids may thus be detected.

$$2KIO_3 + 5H_2SO_3 = I_2 + 3H_2SO_4 + 2KHSO_4 + H_2O.$$

If iodic acid solution be mixed with mucilage of starch, and solution of sulphuretted hydrogen be added, a blue zone is formed at the junction of the liquids.

Ferric iodate, or rather *Oxyiodate* ($Fe_2O4IO_3,8H_2O$), is precipitated on adding solution of ferric chloride to solution of iodate of potassium.

QUESTIONS AND EXERCISES.

462. How may hypochlorous acid be formed?

463. What are the relations of hypochlorous acid to common bleaching-powder?

464. By what reaction is chlorine eliminated from hypochlorites?

465. State the general reaction by which chlorates are formed.

466. Give details of the preparation of chlorate of potassium.

467. Mention the properties of chlorate of potassium.

468. What decompositions occur when chlorate of potassium is heated?

469. Find the molecular weight of chlorate of potassium.

470. What weight of oxygen is yielded when 1 oz. of chlorate of potassium is completely decomposed, and how much chloride of potassium remains?

471. One hundred cubic inches of oxygen, at 60° F. and barometer at 30 inches, weighing 34.203 grains, and 1 gallon containing 277¼ cubic inches, what weight of chlorate of potassium will be required to yield 10 gallons of the gas? *Ans.* 5½ ounces.

472. How many cubic inches of oxygen are producible from 1 oz. of chlorate of potassium?

473. Calculate the weight of chlorate of potassium theoretically obtainable from 100 parts of chloride.

474. How is perchloric acid prepared?

475. Enumerate the chlorine acids.

476. How may the presence of chlorides in chlorates be demonstrated?

477. Mention the tests for chlorates.

478. Give the formula of peroxide of chlorine.

479. What is euchlorine?

480. How may iodic acid be made?

481. Describe the preparation of iodate of potassium.

ACETIC ACID AND OTHER ACETATES.

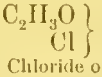
Formula of Acetic Acid $HC_2H_3O_2$, or $H\bar{A}$. Molecular weight 60.

Source.—Acetic acid is said to occur naturally in certain plant juices and animal fluids in minute proportions, but otherwise is an artificial product. Much is furnished by the destructive distillation of wood, hence the term *pyroligneous acid* for the crude product, a hybrid word from *πῦρ*, *pūr*, fire, and *lignum*, wood. This impure product, neutralized by carbonate of sodium, the whole evaporated, and the residue gently heated to drive off the volatile tarry matters, gives acetate of sodium, which after recrystallization furnishes by distillation with oil of vitriol and water acetic acid in a fair state of purity. In Germany and France large quantities of acetic acid are made by the spontaneous oxidation of the alcohol in inferior wines, in the presence, according to Pasteur, of a plant-ferment termed *Mycoderma aceti* (the *Bacterium mycodermi* of Cohn); hence the *white-* and *red-wine vinegar* (*vinegar*, from the French *vin*, wine, and *aigre*, sour). Indeed this bacterium may be propagated, and the artificial manufacture of vinegar from alcohol and water be carried out, by its acid, on a large scale. In England also the domestic form of acetic acid (brown vinegar) has a similar origin: infusion of malt and unmalted grain is fermented, and the resulting oxidation of its sugar, instead of being arrested when the product is an alcoholic liquid, a sort of beer, is allowed to go on to the next stage, acetic acid; it usually contains from 3 to 6 per cent. of real acetic acid ($HC_2H_3O_2$).

Vinegars.—Ordinary brown vinegar contains about 5½ per cent. of acid. The so-called Vinegar of Cantharides (*Acetum Cantharidis*, B. P.) is a solution of the active principle of cantharides in very strong acetic acid, not in vinegar. The Vinegar of Squill (*Acetum Scillæ*, U. S. P.) is also a solution of the active principle of squill in dilute acetic acid, not in true vinegar. The same may be said of *Acetum Lobeliæ*, U. S. P., and *Acetum Sanguinariæ*, U. S. P. (Vinegar of Blood-root). The *Acetum Opii*, U. S. P., or *Black Drop* of America, is made from nutmeg, saffron, and sugar, as well as Opium and Diluted Acetic Acid.

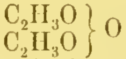
The Acetic Radical.—The group of elements represented by the formula $C_2H_3O_2$ is that characteristic of acetic acid and other acetates, and may, for convenience of study, be assumed to be an acidulous univalent radical. It has not been isolated, unless indeed a compound of similar composition, resulting from the action of peroxide of barium on acetic anhydride, is the radical in question.

Acetyl.—The characteristic grouping in acetates, $C_2H_3O_2$, is frequently considered to contain, rather than to be, a radical—C_2H_3O, termed *acetyl*. Acetates yield a body having the composition C_2H_3OCl, which is regarded as chloride of acetyl; from this may be obtained acetic anhydride ($C_4H_6O_3$), which by absorbing water becomes acetic acid.



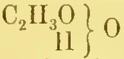
$$\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$$

Chloride of acetyl.



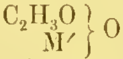
$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$$

Acetic anhydride.



$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

Acetic acid.



$$\left.\begin{matrix}C_2H_3O\\M'\end{matrix}\right\}O$$

Metallic acetates.

The relation of acetic acid to alcohol will be evident from the following equation representing empirically the formation of the acid:—

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O.$$

Acetates in aqueous solution are liable to decomposition. In solution of acetate of morphine a myceloid growth occasionally forms, acetic acid disappears, and morphine is deposited. Solution of acetate of ammonium is liable to a similar change, gradually becoming alkaline.

Synthetical Reaction.

Acetic Acid.

Synthetical Reaction.—To a few grains of acetate of sodium in a test-tube add a little water and some sulphuric acid, and heat the mixture; acetic acid is evolved, and may be condensed by a bent tube adapted to the test-tube by a cork in the usual way.

Acetic Acid.—This is the process by which acetate of sodium or calcium (the neutralized products of the distillation of wood) is made to yield acetic acid on the large scale. As with nitric and hydrochloric acids, the loose term "acetic acid" is that usually applied to aqueous solutions of acetic acid. The *Acidum Aceticum*, U. S. P., contains 36 per cent. of real acid, that is, of $HC_2H_3O_2$; for it contains only 30.6 per cent. of *acetic anhydride* ($C_4H_6O_3$)—still occasionally though somewhat obscurely termed *anhydrous acetic acid*. Its specific gravity is 1.048. *Acidum Aceticum Dilutum*, U. S. P., contains 6 per cent. of $HC_2H_3O_2$. Sp. gr. 1.0083. Glacial acetic acid ($HC_2H_3O_2$) contains no water. It solidifies to a crystalline mass at and below 15° C. (59° F.), hence the appellation *glacial* (from *glacies*, ice). Sp. gr. from 1.056 to 1.058. Good commercial glacial acetic acid (*Acidum Aceticum Glaciale*, U. S. P.) does not contain more than 1 per cent. of water, corresponding to 84.15 per cent. of acetic anhydride. Although water is lighter than this acetic acid, yet the addition of water at first renders the acid heavier; evidently therefore condensation, or contraction in bulk, occurs on mixing the liquids: after 10 per cent. has been added, the addition of more water produces the usual effect of dilution of a heavy liquid by a lighter, namely, reduction of relative weight. This matter will be better understood after the subject of specific gravity has been studied.

The following equation is expressive of the foregoing reaction:—

$$\begin{array}{ccccccc} NaC_2H_3O_2 & + & H_2SO_4 & = & HC_2H_3O_2 & + & NaHSO_4 \\ \text{Acetate of} & & \text{Sulphuric} & & \text{Acetic acid.} & & \text{Acid sulphate} \\ \text{sodium.} & & \text{acid.} & & & & \text{of sodium.} \end{array}$$

or, assuming the existence of acetyl (C_2H_3O) in acetic acid, and a corresponding radical sulphuryl (SO_2) in sulphuric acid—

$$\left.\begin{matrix} C_2H_3O \\ Na \end{matrix}\right\} O + \left.\begin{matrix} SO_2 \\ H_2 \end{matrix}\right\} O_2 = \left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O + \left.\begin{matrix} SO_2 \\ NaH \end{matrix}\right\} O_2;$$

or, thirdly, on the assumption that salts contain the oxide of a basylous radical united with the anhydride of an acid (the old view under which such names as acetate of soda were formed)—

$$Na_2O,C_4H_6O_3 + 2H_2O,SO_3 = Na_2O,H_2O,2SO_3 + H_2O,C_4H_6O_3.$$

Note on the Constitution of Salts.

Which of these three equations, or, more broadly, which of the three views of the constitution of salts illustrated by the equations, is correct, it is impossible to say. Whether it is $C_2H_3O_2$, C_2H_3O, or $C_4H_6O_3$, which migrates from one acetic compound to another, whether it is SO_4, SO_2, or SO_3, which migrates from one sulphuric compound to another, and so on with other acidulous groupings, cannot at present be determined. There are strong objections to each view; and possibly neither is right. Either the given radicals cannot be isolated, or application of the forces of heat, light, and electricity do not confirm views arrived at by the results of operations with the chemical force; or a salt comes to be regarded as having so large a number of constituent parts that the view, however true, breaks down in practice from the sheer inability of the mind to grasp the complicated analogies involved. Yet for the purposes of description, study, and conversation some system must be adopted. Let the first, then, be generally taken, over-reliance on it being checked by the use of general instead of special names for the hypothetical radicals, and other systems be employed in certain cases. (See also p. 283.)

Analytical Reactions (Tests).

First Analytical Reaction.—To an acetate add sulphuric acid and heat the mixture; acetic acid, recognized by its odor, is evolved.

Note 1.—Iodine, sulphurous acid, and other substances of powerful odor, mask that of acetic acid; they must be removed, therefore, usually by precipitation or oxidation, before applying this test.

Note 2.—It will be noticed that this reaction is identical with the previous one; it has synthetical or analytical interest, according to the object and method of its performance.

Second Analytical Reaction.—Repeat the above action, a few drops of spirit of wine being first added to the acetate; acetic ether (acetate of ethyl, $C_2H_5C_2H_3O_2$), also of characteristic odor, is evolved.

The basylous radical ethyl (C_2H_5) will be referred to subsequently.

Third Analytical Reaction.—Heat a fragment of a dry acetate in a test-tube, and again notice the odor of the gaseous products of the decomposition; among them is *acetone* (C_3H_6O), the smell of which is characteristic. Carbonate of the metal remains in the test-tube.

Fourth Analytical Reaction.—To a solution of an acetate made neutral by the addition of acid or alkali, as the case may be, add a few drops of neutral solution of perchloride of iron; a deep-red liquid results, owing to the formation of ferric acetate ($Fe_26C_2H_3O_2$). Boil; a precipitate of oxyacetate of iron occurs, leaving the liquid colorless. Strong acids also decompose ferric acetate.

Analytical Note.—It will be noticed that the formation of characteristic precipitates, the usual method of removing radicals from solution for recognition, is not carried out in the qualitative analysis of acetates. This is because all acetates are soluble. Acetate of silver ($AgC_2H_3O_2$) and mercurous acetate ($HgC_2H_3O_2$) are only sparingly soluble in cold water, but the fact can seldom be utilized in analysis. Hence peculiarities of color and odor, the next best characters on which to rely, are adopted as means by which acetates may be detected. Acetates, like other organic compounds, char when heated to a high temperature.

Note on Anhydrides.—Up to this point the student has regarded an anhydride as a body derived from an acid by removal of the *whole* of the hydrogen of the acid, together with as much of its oxygen as with the hydrogen forms water. The definition will scarcely apply to acetic anhydride, and must therefore be somewhat qualified. An *anhydride* is derived from an acid, the acid having lost the whole of its *basylous* hydrogen and so much oxygen as is necessary to form water with that hydrogen. Anhydrides are obtained by heating acids, and by other methods.

QUESTIONS AND EXERCISES.

482. What is the formula of acetic acid?
483. State the relation of acetic acid to other acetates.
484. What is the molecular weight of acetic acid?
485. Name the sources of acetic acid.
486. What is pyroligneous acid?
487. From what compound is the acetic acid of foreign and English vinegar immediately derived?
488. How much real acid is contained in official vinegar?
489. What is the nature of the "Vinegars" of Pharmacy?
490. How may acetic acid be obtained from acetate of sodium?
491. How much real acid is contained in the official acetic acid?
492. Mention the strength of commercial glacial acetic acid.
493. Give three or more views of the constitution of acetates, illustrating each by formulæ.
494. Enumerate the tests for acetates.

HYDROSULPHURIC ACID AND OTHER SULPHIDES.

Formula of Hydrosulphuric Acid H_2S. Molecular weight 34.

Source and Varieties of Sulphur.—The acidulous radical of *hydrosulphuric acid*, *sulphydric acid*, or *sulphuretted hydrogen*, and other sulphides, is the element sulphur (S). It occurs in nature in combination with metals, as already stated in describing the ores of some of the metals, and also in the free state. Most of the sulphur used in medicine is imported from Sicily, where it occurs chiefly associated with blue clay. It is purified by fusion, sublimation, or distillation. Melted and poured into moulds, it constitutes a crystalline mass termed *roll sulphur.* If distilled and the vapor carried into large chambers, so that it may be rapidly condensed, the crystals are so minute as to give the sulphur a pulverulent character; this is *sublimed sulphur* (*Sulphur Sublimatum*, U. S. P.) or *flowers of sulphur:* the same washed with dilute ammonia, to remove traces of sulphuric acid, or, possibly, arsenious sulphide, constitutes *Sulphur Lotum*, U. S. P.

The third common form, *milk of sulphur*, will be noticed subsequently. Sulphur also occurs in nature in combination as a constituent of animal and vegetable tissues, as sulphurous acid gas (SO_2) in volcanic vapors, and as sulphuretted hydrogen in some waters, as those of Harrogate.

Plastic sulphur is one of the allotropic varieties of the element, obtained on heating sulphur considerably beyond its melting-point and pouring into cold water.

Quantivalence.—Sulphur is sexivalent, as seen in sulphuric anhydride (SO_3), a substance which will be noticed under sulphuric acid. It also occasionally exhibits quadrivalent (SO_2) and still oftener bivalent affinities (H_2S).

Molecular Weight.—At very high temperatures sulphur follows the rule that, under similar conditions of heat and pressure, atomic weights (in grammes, grains, etc.) of volatile elements occupy equal volumes of vapor; its formula therefore is S_2, and molecular weight 64. At lower temperatures the volume weighs three times as much as it should do if following usual laws, and then the molecule would appear to contain six atoms (S_6).

Acid Salts.—Sulphur (S'') being the first acidulous radical of bivalent activity met with in these sections on acids, it is desirable here to draw attention to a new class of salts to which such a radical will generally give rise. These are acid salts, which are intermediate between normal salts and acids. Univalent radicals with an atom of hydrogen give an acid, and with an atom of other basylous radicals an ordinary or normal salt. But bivalent radicals, from the fact that they give with two atoms of hydrogen an acid, and with two atoms of univalent metals a normal salt, may obviously give intermediate bodies containing one atom of hydrogen and one atom of metal: these are appropriately termed acid salts: they are neither normal acids nor normal salts, but *acid salts.* (Examples: $KHCO_3$, $NaHSO_4$, $KHC_4H_4O_6$, Na_2HPO_4, $CuHAsO_3$, CaH_42PO_4.) Whether or not these salts give an acid reaction with blue litmus-paper depends on the strength of the respective radicals. Usually they do redden the test-paper, but sometimes not; thus the acid sulphide or sulphydrate of potassium (KHS), of sodium (NaHS), or ammonium (AmHS) has alkaline properties.*

The chemical analogy between sulphur and oxygen, already once alluded to (p. 173), is further illustrated by the compounds just mentioned. Sulphur is also closely related to the rarer element Selenium. Thus we have SeO_2 as well as SO_2, H_2SeO_3 (selenious acid) as well as H_2SO_3 (sulphurous acid), H_2SeO_4 (selenic acid) as well as H_2SO_4 (sulphuric acid). The rare element Tellurium also seems to have similar analogies. The four hydrogen compounds of the group have the formulæ H_2O, H_2S, H_2Se, H_2Te.

Synthetical Reactions.

Sulphuretted Hydrogen.

First Synthetical Reaction: The preparation of sulphuretted hydrogen.—This operation was described on page 95, and probably has already been studied by the reader.

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* Some chemists regard these sulphydrates as compounds of basylous radicals with HS, a univalent grouping termed hydrosulphyl (persulphide of hydrogen, H_2S_2), just as hydrates are similarly viewed as compounds of the univalent radical hydroxyl (HO) (peroxide of hydrogen, H_2O_2)—H_2S becoming HHS or HHs (hydrosulphylide of hydrogen), and H_2O becoming HHO or HHo (hydroxylide of hydrogen).

Precipitated Sulphur.

Second Synthetical Reaction.—Prepare the variety of the radical of sulphides known as *Precipitated Sulphur* (*Sulphur Præcipitatum*, U. S. P.), or *milk* of sulphur, by boiling a few grains of flowers of sulphur (100 parts) with slaked lime (66 parts) and some water (500 parts) in a test-tube (larger quantities in an evaporating-basin), filtering, and (reserving a small portion of the filtrate) adding dilute hydrochloric acid until the well-stirred milklike liquid has still a faint alkaline reaction on test-paper; sulphur is precipitated, and may be collected on a filter, washed and dried (at about 120°). Excess of acid must be avoided, or some hydrosulphyl, the liquid persulphide of hydrogen (H_2S_2), will be formed, probably causing the particles of sulphur to aggregate to a gummy mass.

This is the process of the Pharmaeopœias. Polysulphide of calcium and hyposulphite of calcium are formed :—

$$\underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{3CaH_2O_2} + \underset{\text{Sulphur.}}{6S_2} = \underset{\substack{\text{Polysulphide}\\ \text{of calcium.}}}{2CaS_5} + \underset{\substack{\text{Hyposulphite}\\ \text{of calcium.}}}{CaS_2O_3} + \underset{\text{Water.}}{3H_2O}$$

On adding the acid, both salts are decomposed and, after an intermediate reaction, sulphur separates :—

$$\underset{\substack{\text{Polysulphide}\\ \text{of calcium.}}}{2CaS_5} + \underset{\substack{\text{Hyposulphite}\\ \text{of calcium.}}}{CaS_2O_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl} = \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{3CaCl_2} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Sulphur.}}{6S_2}$$

The polysulphide of calcium yields sulphuretted hydrogen and milk-white sulphur on the addition of acid. The hyposulphite of calcium then yields sulphurous acid gas as well as a yellowish sulphur. The gases react and give sulphur and water, very little sulphuretted hydrogen escaping. A little pentathionic acid (see Index) is also said to be formed.

$$4H_2S + 2SO_2 = 3S_2 + 4H_2O.$$

Calcareous Precipitated Sulphur: The *old* "Milk of Sulphur."—To a sulphur solution prepared as before (or to the reserved portion) add a little dilute sulphuric acid; the precipitate is in this case largely mixed with sulphate of calcium :—

$$\underset{\substack{\text{Polysulphide}\\ \text{of calcium.}}}{2CaS_5} + \underset{\substack{\text{Hyposulphite}\\ \text{of calcium.}}}{CaS_2O_3} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{3H_2SO_4} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Sulphate of}\\ \text{calcium.}}}{3(CaSO_4,2H_2O)}$$
$$+ \underset{\text{Sulphur.}}{6S_2}$$

Place a little of each of these specimens of precipitated sulphur with a drop of the supernatant liquid on a strip of glass, cover each spot with a piece of thin glass, and examine the precipitates under a microscope; the pure sulphur will be found to consist of minute grains or globules, the calcareous to contain comparatively large crystals (sulphate of calcium).

Note.—A large proportion of the precipitated sulphur met with in trade in England still is thus mixed with sulphate of calcium, most of such specimens containing two-thirds of their weight of that substance. Many purchasers, indeed, are so accustomed to the satiny appearance of the mixed article as to regard the real sulphur with suspicion, sometimes refusing to purchase it. The mixed article is, certainly, more easily mixable with aqueous liquids; but it has long been discarded from the Pharmacopœias of Great Britain, and, on the whole, is scarcely worthy of a prominent place in the pharmacy of 1883.

Many English pharmacists have ceased to sell any sulphur which yields a white ash (the anhydrous sulphate) when a little is burnt off on the end of a table-knife or spatula. (No more damage is done to the steel than a rub on a knife-board will remove.)

To ascertain exactly the amount of sulphate of calcium in a specimen of calcareous precipitated sulphur, place a weighed quantity in a tared crucible and heat till no more vapors are evolved. The weight of the residual anhydrous sulphate of calcium ($CaSO_4 = 136$), with one-fourth thereof added, is the amount of crystalline sulphate of calcium ($CaSO_4,2H_2O = 172$) present in the original quantity of calcareous sulphur.

Analytical Reactions (Tests).

To a sulphide add a few drops of hydrochloric acid; sulphuretted hydrogen will probably be evolved, well known by its smell. If the sulphide is not acted upon by the acid, or if free sulphur be under examination, mix a minute portion with a fragment of solid caustic potash or soda and fuse on a silver coin or spoon. When cold, place a drop of dilute hydrochloric acid on the spot; sulphuretted hydrogen is evolved, and a black stain, due to sulphide of silver (Ag_2S), left on the coin.

Other sulphur reactions may be adopted as tests, but the above are sufficient for all ordinary purposes. The most convenient reagent for detecting a sulphide in solution of ammonia is ammonio-sulphate of copper, which gives a black precipitate of sulphide of copper if a sulphide be present.

The *Iodide of Sulphur* (S_2I_2) has been mentioned under "Iodine." A chloride (S_2Cl_2) and bromide (S_2Br_2) may also be formed from their elements. A mixture of sulphur and chloride of sulphur is sometimes met with under the name of *hypochloride of sulphur.*

QUESTIONS AND EXERCISES.

495. In what form does sulphur occur in nature?

496. State the modes of preparation of the three chief commercial varieties of sulphur.

497. To what extent does the atom of sulphur vary in quantivalence?

498. State the relations of acid salts to acids and to normal salts.

499. Define sulphides and sulphydrates.

500. Describe the preparation of sulphuretted hydrogen.

501. What are the characters of pure precipitated sulphur?

502. Give equations explanatory of the reactions which occur in precipitating sulphur according to the official process.

503. Describe the microscopic test for calcareous precipitated sulphur.

504. Mention a ready physical method of detecting sulphate of calcium in precipitated sulphur.

505. Mention the tests for sulphides, and the character by which sulphuretted hydrogen is distinguished from other sulphides.

506. How are sulphides insoluble in acids tested for sulphur?

507. Give a method for the detection of a trace of sulphur in solution of ammonia.

SULPHUROUS ACID AND OTHER SULPHITES.

Formula of Sulphurous Acid H_2SO_3. Formula of sulphurous acid gas or sulphurous anhydride, commonly termed sulphurous acid, SO_2. Molecular weight of sulphurous acid 82; of the anhydride 64.

When sulphur is burned in the air it combines with oxygen and forms sulphurous acid gas (SO_2), more correctly termed sulphurous anhydride, or commonly, but erroneously, sulphurous acid. It is a pungent, colorless gas, readily liquefied on being passed through a tube externally cooled by a *freezing-mixture* composed of two parts of well-powdered ice (or, better, snow) with one part of common salt. If sulphurous acid gas becomes moist or is passed into water, heat is evolved and true sulphurous acid (H_2SO_3) formed. The latter body may be obtained in crystals; but it is very unstable, and hence the properties of the sulphurous radical must be studied under the form of some other sulphite; sulphite of calcium ($CaSO_3$) or sulphite of sodium (Na_2SO_3) may be used for the purpose.

Quantivalence.—The radical of the sulphite is bivalent (SO_3''), and hence forms acid sulphites, such as acid sulphite of potassium ($KHSO_3$) and normal sulphites, such as sulphite of sodium (Na_2SO_3).

Note on Nomenclature.—The sulphites are so named from the usual rule, that salts corresponding with acids whose names end in *ous* have a name ending in *ite.* They are generally made by passing sulphurous acid gas over moist oxides or carbonates; in the latter case carbonic acid gas escapes.

Synthetical Reaction.—To a few drops of sulphuric acid in a test-tube add a piece of charcoal and apply heat; sulphurous acid gas is evolved, and may be conveyed by a bent tube into a small quantity of cold water in another test-tube. Larger quantities may be made in a Florence flask. The product is the *Acidum Sulphurosum*, U. S. P. It contains about 4.5 per cent. of sulphurous acid (H_2SO_3) or about 3.5 per cent. of the gas (SO_2). The process is also that described in the Pharmacopœia, except that the gas is purified by passing through a small wash-bottle before final collection. Specific gravity 1.022 to 1.023.

$$\underset{\text{Sulphuric acid.}}{4H_2SO_4} + \underset{\text{Carbon (charcoal).}}{C_2} = \underset{\text{Carbonic acid gas.}}{2CO_2} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Sulphurous acid gas.}}{4SO_2}$$

Sulphurous acid gas may also be made by boiling copper, mercury, or iron with sulphuric acid, sulphate of the metals being formed. Also by boiling sulphur with sulphuric acid.

$$\underset{\text{Sulphurous acid gas.}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphurous acid.}}{H_2SO_3}$$

If in this process the water were replaced by solutions of or solid metallic oxides or carbonates, sulphites of the various metals would be formed. The formula of sulphite of potassium (*Potassii Sulphis*, U. S. P.) is $K_2SO_3,2H_2O$; of sulphite of sodium (*Sodii Sulphis*, U. S. P.), $Na_2SO_3,7H_2O$; of the bisulphite or acid sulphite, $NaHSO_3$ (*Sodii Bisulphis*, U. S. P.). Under the name of *antichlor* the former is used for removing traces of chlorine from paper pulp. The sulphite of magnesium (*Magnesii Sulphis*, U. S. P., $MgSO_3,6H_2O$) is deposited as a white crystalline powder from the aqueous solution containing excess of sulphurous acid. The so-called *Bisulphite of Lime*, employed by brewers for retarding or arresting fermentation and oxidation, and used for various antiseptic purposes, is a solution of sulphite of calcium ($CaSO_3$) in free sulphurous acid (H_2SO_3), and is made by passing sulphurous acid gas (SO_2) into thin milk of lime. Its specific gravity varies from 1.050 to 1.070, and its potential strength of anhydride (SO_2) from 4 to 6 per cent.

Analytical Reactions (Tests).

First Analytical Reaction.—To a sulphite (of sodium, for instance, made by passing sulphurous acid into solution of carbonate of sodium) add a drop or two of dilute hydrochloric acid; sulphurous acid gas escapes, recognized by a peculiar pungent smell.

This smell is the same as that evolved on burning lucifer matches that have been tipped with sulphur. It is due, probably, not to the gas (SO_2), but to sulphurous acid (H_2SO_3) formed by the union of sulphurous acid gas with either the moisture of the air or that on the surface of the mucous membrane of the nose. The gas is highly suffocating.

Second Analytical Reaction.—To a sulphite add a little water, a fragment or two of zinc, and then hydrochloric acid; sulphuretted hydrogen will be evolved, known by its putrid odor and action on a piece of paper placed like a cap on the mouth of the test-tube, and moistened with a drop of solution of acetate of lead, black sulphide of lead being formed. Sulphurous acid may be detected in acetic acid, or in hydrochloric acid, by this test.

$$H_2SO_3 + H_6 = H_2S + 3H_2O.$$

Other Analytical Reactions.

To solutions of neutral sulphites add nitrate or chloride of barium, chloride of calcium, or nitrate of silver; in each case white sulphites of the various metals are precipitated. The barium sulphite is soluble in weak hydrochloric acid; but if a drop or two of chlorine-water is first added, barium sulphate is formed, which is insoluble in acids. The other precipitates are also soluble in acids. The silver sulphite is decomposed on boiling, sulphuric acid being formed, and metallic silver set free, the mixture darkening in color.

To recognize the three radicals in an aqueous solution of sulphides, sulphites, and sulphates, add chloride of barium, filter, and wash the precipitate. In the filtrate, sulphides are detected by the sulphuretted hydrogen evolved on adding an acid. In the precipitate, sulphites are detected by the odor of sulphurous acid produced on adding hydrochloric acid, and sulphates by their insolubility in the acid.

QUESTIONS AND EXERCISES.

508. What are the differences between sulphurous acid and sulphurous acid gas, sulphites and acid sulphites?

509. State the characters of sulphurous acid gas?

510. How is the official Sulphurous Acid prepared?

511. By what test may sulphurous acid be recognized in acetic acid?

512. Give a method by which sulphites may be detected in presence of sulphides and sulphates.

SULPHURIC ACID AND OTHER SULPHATES.

Formula of Sulphuric Acid H_2SO_4. Molecular weight 98.

Many sulphates occur in nature: but the common and highly important hydrogen sulphate, sulphuric acid, is made artificially.

Preparation of the Acid: General Nature of the Process.—Sulphur itself, or sometimes the sulphur in iron pyrites, is first converted into sulphurous acid gas by burning in air, and this gas, by moisture and oxygen, into sulphuric acid ($SO_2 + H_2O + O = H_2SO_4$).

Details of the Process.—The oxygen necessary to oxidize the sulphurous acid gas cannot directly be obtained from air, but indirectly, the agency of nitric oxide (NO) being employed—this gas becoming nitric peroxide (NO_2) by the action of the air, and the nitric peroxide again becoming nitric oxide by the action of the sulphurous acid gas, and so on. A small quantity of nitric oxide gas will in this way act as carrier of oxygen from the air to very large quantities of sulphurous acid.

The following equations represent the successive steps:—

$$\underset{\text{Sulphur.}}{S_2} + \underset{\substack{\text{Oxygen}\\\text{(of the air).}}}{2O_2} = \underset{\substack{\text{Sulphurous.}\\\text{acid gas.}}}{2SO_2}$$

$$\underset{\substack{\text{Sulphurous}\\\text{acid gas.}}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3}$$

$$\underset{\substack{\text{Nitric}\\\text{oxide.}}}{2NO} + \underset{\substack{\text{Oxygen}\\\text{(of the air).}}}{O_2} = \underset{\substack{\text{Nitric}\\\text{peroxide.}}}{2NO_2}$$

$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3} + \underset{\substack{\text{Nitric}\\\text{peroxide.}}}{NO_2} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{NO}$$

On the large scale the sulphurous acid gas is produced by burning sulphur in furnaces; it is carried, together with the nitric vapors, by flues into leaden chambers, where jets of steam supply the necessary moisture; the steam also, condensing, prevents other reactions. The resulting dilute sulphuric acid is concentrated by evaporation in leaden vessels.

The nitric oxide is in the first instance obtained from nitric acid, and this from nitrate of potassium or of sodium by the action of a small quantity of the sulphuric acid of a previous operation.

$$\underset{\substack{\text{Nitrate of}\\\text{sodium.}}}{2NaNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate of}\\\text{sodium.}}}{Na_2SO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3}$$

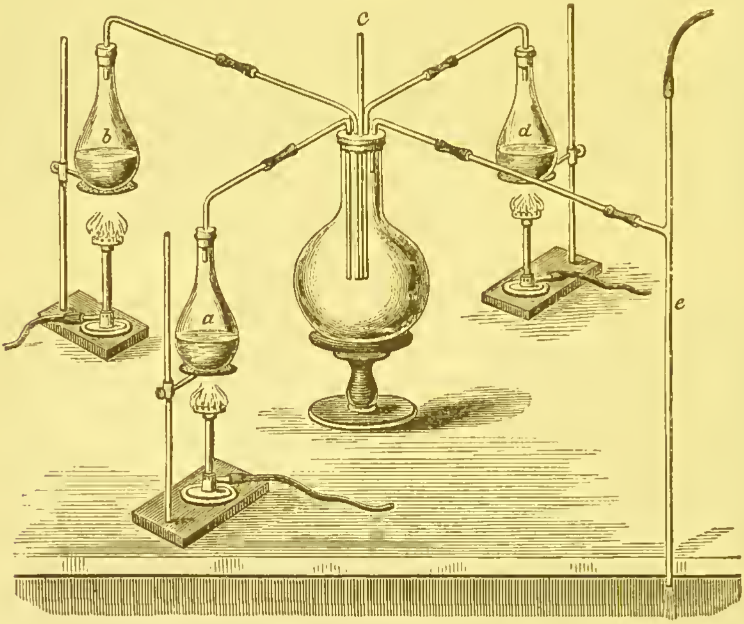
$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{3H_2SO_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{2NO}$$

Other Processes.—Sulphuric acid may be obtained by other processes, as by distilling the sulphate of iron resulting from the natural oxidation of iron pyrites by air; but it is seldom so made at the present day. The sulphate of iron was formerly called *green vitriol* (p. 141), and the distilled product *oil of vitriol;* the latter in allusion to its consistence and origin.

Experiment.—For purposes of practical study, a small quantity may be made (as shown in fig. 39) by passing, *a*, sulphurous acid gas

(p. 302), *b*, nitric oxide in small quantity (p. 286), *c*, air (forced through by aid of bellows or a gas-holder or drawn through by a *water-aspirator*, *e*), and occasionally, *d*, steam (generated in a Florence flask) through glass tubes, nearly to the bottom of a two- or three-quart flask.

Fig. 39.



Experimental Manufacture of Sulphuric Acid.

$$SO_2 + H_2O = H_2SO_3 ; \quad | \quad 2NO + O_2 = 2NO_2 ;$$
$$H_2SO_3 + NO_2 = H_2SO_4 + NO.$$

A slow current of sulphurous acid gas, air, and steam, and a small quantity of nitric oxide, will furnish, in the course of a few minutes, enough sulphuric acid for recognition by the first of the following analytical reactions. The manufacturing process may be more exactly imitated by burning sulphur in a tube placed where the flask *a* is represented in the foregoing figure, or by burning it under a funnel there attached; but in either of these cases strong aspiration must be maintained.

Purification.—Sulphuric acid may contain arsenic, nitrous compounds, and salts. Arsenic may be detected by the hydrogen-test (p. 170), nitrous compounds by powdered sulphate of iron (which acquires a violet tint if they are present), and salts by the residue left on boiling a little to dryness in a crucible in a fume-chamber. If only nitrous compounds are present, the acid may be purified by heating with about one-half per cent. of sulphate of ammonium—water and nitrogen being produced (Pelouze). If arsenic occurs, boil with a small quantity of hydrochloric acid, which converts the arsenic into chloride of arsenicum; or heat with a little nitric acid, which converts arsenious (As_2O_3) into arsenic anhydride (As_2O_5), then add sulphate of ammonium, and distil in a retort containing pieces of quartz and heat by an annular-shaped burner (to prevent "bumping;" see p. 277). The arsenic anhydride remains in the retort. (Arsenious anhydride would be carried over with the sulphuric acid vapors.) By distillation the acid is also purified from salts (such as $NaHSO_4$) which are not volatile.

Quantivalence.—The sulphuric radical being bivalent (SO_4''), acid as well as normal sulphates may exist. Acid sulphate of potassium ($KHSO_4$) is an illustration of the former, sulphate of sodium (Na_2SO_4) of the latter; *double sulphates* may also occur, such as that of potassium and magnesium ($K_2SO_4,MgSO_4,6H_2O$). Sulphates generally contain water of crystallization.

Pure sulphuric acid (H_2SO_4) is of specific gravity 1.848. The best "oil of vitriol" of commerce, a colorless liquid of oily consistence, is of specific gravity 1.843, and contains 96.8 per cent. of real acid (H_2SO_4). The *Acidum Sulphuricum*, U. S. P., should contain not less than 96 per cent. of H_2SO_4, and have a sp. gr. not below 1.840. The *Acidum Sulphuricum Dilutum*, U. S. P., contains 10 per cent. of the strong acid, and should have a sp. gr. of nearly 1.067. The *Acidum Sulphuricum Aromaticum*, U. S. P., a dilute acid in which are dissolved oil of cinnamon and tincture of ginger, contains about 20 per cent. of strong acid, sp. gr. 0.955. There are some definite compounds of sulphuric acid with water; the first (H_2SO_4,H_2O) may be obtained in crystals.

Sulphuric anhydride (SO_3) is a white silky crystalline solid, having no acid properties. It is made by distilling sulphuric acid with phosphoric anhydride ($3H_2SO_4 + P_2O_5 = 2H_3PO_4 + 3SO_3$). It appears to unite with sulphuric acid and some other normal sulphates to form compounds (R'_2SO_4,SO_3) resembling in constitution red chromate of potassium or borax. The fuming sulphuric acid (H_2SO_4,SO_3), formerly made at Nordhausen in Saxony, seems to be such a body.

Note.—Sulphuric acid is a most valuable compound to all chemists and manufacturers of chemical substances. By its agency, direct or indirect, many, if not most, chemical transformations are effected. To describe all its uses would be to write a work on chemistry.

Analytical Reactions (Tests).

First Analytical Reaction.—To a solution of a sulphate add solution of a barium salt; a white precipitate of sulphate of barium ($BaSO_4$) falls. Add nitric acid and boil the mixture; the precipitate does not dissolve.

This reaction is as highly characteristic of sulphate as it has been stated to be of barium salts (*vide* page 102). The only error likely to be made in its application is that of overlooking the fact that nitrate and chloride of barium are less soluble in strong acid than in water. On adding the barium salt to the acid liquid, therefore, a white precipitate may be obtained, which is simply the nitrate or chloride of barium. The appearance of such a precipitate differs considerably from that of the barium sulphate, hence a careful operator will not be misled. Should any doubt remain, water should be added, which will dissolve the nitrate or chloride, but not affect the sulphate.

Second Analytical Reaction.—Mix a fragment of an insoluble sulphate ($BaSO_4$, *e. g.*) with carbonate of potassium or of sodium; or, better, with both carbonates, and fuse the mixture in a small crucible. Digest the residue when cold, in water, and filter; the filtrate may be tested for the sulphuric radical.

This is a convenient method of qualitatively analyzing insoluble sulphates, such as those of barium and lead.

Third Analytical Reaction.—Mix a fragment of an insoluble sulphate with a little alkaline carbonate on a piece of charcoal, taking care that some of the charcoal-dust is included in the mixture. Heat the little heap in the blowpipe-flame until it fuses, and, when cold, add a drop of acid; sulphuretted hydrogen is evolved, recognized by its odor.

This is another process for the recognition of insoluble sulphates. Other preparations of sulphur, and sulphur itself, give a similar result. It is therefore rather a test for sulphur and its compounds than sulphates only; but the absence of other salts can generally, if necessary, be previously determined.

Note.—The presence of the sulphuric radical in a solution having been proved by the above reactions, its occurrence as the normal sulphate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper, and the detection of the metal—its occurrence as sulphuric acid or an acid sulphate by the sourness of the liquid to the taste and the effervescence produced on the addition of a carbonate.

Antidote.—In cases of poisoning by strong sulphuric acid, solution of carbonate of sodium (common washing-soda), magnesia and water, etc., may be administered as antidotes.

QUESTIONS AND EXERCISES.

513. What is the formula of sulphuric acid, and what its molecular weight?

514. How is it related to other sulphates?

515. Write a short article on the manufacture of sulphuric acid, giving either diagrams or equations.

516. How may nitrous compounds be detected in, and eliminated from, sulphuric acid?

517. State the method by which the presence of arsenic is detected in sulphuric acid, and explain the process by which it may be removed.

518. Define sulphates, acid sulphates, and double sulphates.

519. What percentage of real acid is contained in commercial oil or vitriol?

520. State the strength of the official "diluted" and "aromatic" sulphuric acid.

521. By what process is sulphuric anhydride obtained from Nordhausen sulphuric acid?

522. Explain the reactions which occur in testing for sulphates.

523. Ascertain by calculation the weight of oil of vitriol (of 96.8 per cent.) necessary for the production of one ton of dry sulphate of ammonium.—*Ans.* 1718 pounds.

524. Name the antidotes in cases of poisoning by strong sulphuric acid.

CARBONIC ACID AND OTHER CARBONATES.

Formula of Carbonic Acid H_2CO_3. Molecular weight 62. Formula of carbonic acid gas, or carbonic anhydride, commonly termed carbonic acid, CO_2.

Sources.—Carbonates (compounds containing the grouping CO_3) are very common in nature, the calcium carbonate ($CaCO_3$) being widely distributed as chalk, limestone, or marble. The hydrogen carbonate, true carbonic acid, is not known, unless indeed carbonic acid gas assumes that condition on dissolving in water. Such a solution (see page 85) changes the color of blue litmus-paper. and the gas does not; this may be because only the true acid (H_2CO_3) affects the litmus, or because the gas (CO_2) cannot come into real contact with the litmus without a medium. From the commonest natural carbonate, carbonate of calcium, are derived the carbonic constituents of the one most frequently used in medicine and in the arts generally, carbonate of sodium.

Carbonate of sodium is prepared, by "the Leblanc process," from the chief natural salt, the chloride. After the chloride has been converted into sulphate (salt-cake) by sulphuric acid (or by sulphurous acid, air, and steam—Hargreave's modification)—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

the sulphate is roasted with limestone and small coal, by which carbonate of sodium and sulphide of calcium are formed:—

$$Na_2SO_4 + C_4 + CaCO_3 = CaS + Na_2CO_3 + 4CO.$$

Carbonic oxide gas and a little carbonic acid gas from the excess of chalk escape; the residual mass (black ash) is digested in water, in which the carbonate of sodium dissolves, the sulphide of calcium with a little oxide remaining insoluble. The solution is evaporated to dryness, and yields true carbonate of sodium. This is roasted with a small quantity of sawdust, to convert any caustic soda, resulting from the action of the lime on the carbonate, into normal carbonate. The product is *soda-ash.* Dissolved in water and crystallized, it constitutes the ordinary "soda" used for washing purposes; recrystallized and sometimes ground, it forms the official carbonate of sodium (*Sodii Carbonas*, U. S. P.) ($Na_2CO_3,10H_2O$). The reaction is rendered more intelligible by regarding it as occurring in two stages: 1st, the reduction of the sulphate of sodium to sulphide by the carbon of the coal—

$$Na_2SO_4 + C_4 = Na_2S + 4CO;$$

2d, the reaction of the sulphide of sodium and carbonate of calcium, giving soluble carbonate of sodium, thus—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The sulphur in the residual sulphide (or, perhaps, oxysulphide) of calcium may be recovered by exposure to air, and the subsequent action of hydrochloric acid. Some hyposulphite of calcium (CaS_2O_3) is first formed, and the action of the acid on this and on undecomposed sulphide gives chloride of calcium, water, and sulphur. A more promising process of recovery is that by Schaffner and Helbig. It consists in decomposing the calcium sulphide by magnesium chloride, burning the resulting sulphuretted hydrogen to sulphurous acid gas and regenerating the magnesium chloride:—

$$(1)\quad CaS + MgCl_2 + 2H_2O = H_2S + CaCl_2 + Mg2HO;$$
$$(2)\quad CaCl_2 + Mg2HO + CO_2 = MgCl_2 + CaCO_3 + H_2O.$$

Another Process.—To a strong solution of common salt, bicarbonate of ammonium is added, when a precipitate of bicarbonate of sodium occurs. The resulting chloride of ammonium may be converted into carbonate by heating with chalk, and the carbonate be more fully carbonated by carbonic acid gas obtained by heating the bicarbonate of sodium, which is thereby reduced to the ordinary neutral carbonate. This method is known as "the ammonia process."

Carbonic acid gas (CO_2) is a product of the combustion of all carbonaceous matters. It is constantly exhaled by animals and inhaled by plants, its intermediate storehouse being the atmosphere, throughout which it is equally distributed by *diffusion* (*vide* p. 24) to the extent of about 4 parts in 10,000. A larger proportion than that just mentioned gives to confined air depressing effects, 4 or 5 per cent. rendering the atmosphere poisonous when taken into the blood from the lungs. Carbonic acid, however, may be taken into the stomach with beneficial sedative effects; hence, probably, much of the value of such effervescing liquids as soda-water, lemonade, and solutions of the various granulated preparations and effervescing powders (*vide* p. 86). The gas liquefies on being compressed, and the liquid solidifies on being evolved. Carbonic acid gas is twenty-two times as heavy as hydrogen, and about half as heavy again as air.

Sulphocarbonates resemble carbonates in constitution, but contain sulphur in place of oxygen.

Sulphocarbonic anhydride, CS_2, commonly termed *bisulphide of carbon* or *disulphide of carbon* (*Carbonei Bisulphidum*, U. S. P.), is a highly volatile and inflammable liquid, easily made from its elements. Sp. gr. 1.272; boiling-point 46° C. It may be rendered almost scentless by digestion with copper turnings. Its possible impurities are dissolved sulphur, sulphur oils, and sulphuretted hydrogen.

REACTIONS.

Synthetical and Analytical Reactions.—1. To a fragment of marble in a test-tube add water and then hydrochloric acid; carbonic acid gas (CO_2) is evolved, and may be conveyed into water or solutions of salts by the usual delivery-tube.

This is the process of the British Pharmacopœia, and the one usually adopted for experimental purposes. Passed into carbonate of sodium, the gas gives *Sodii Bicarbonas* (p. 82), and into carbonate of potassium, *Potassii Bicarbonas* (p. 70). On the large scale the gas is prepared from chalk or marble and sulphuric acid, frequent stirring promoting its escape.

2. Pass the gas into lime-water; a white precipitate of carbonate of calcium ($CaCO_3$) falls. Solution of subacetate of lead may be used instead of, and is perhaps even a more delicate test than, lime-water.

The evolution of a gas on adding an acid to a salt, warming the mixture if necessary, the gas being inodorous and giving a white precipitate with lime-water, is sufficient evidence of the presence of a carbonate. Carbonates in solution of ammonia, potash, or soda may be detected by the direct addition of solution of lime. Carbonates in presence of sulphites or hyposulphites may be detected by adding acid tartrate of potassium, which decomposes carbonates with effervescence, but does not attack sulphites or hyposulphites.

3. Blow air from the lungs through a glass tube into lime-water; the presence of carbonic acid gas is at once indicated.

The passage of a considerable quantity of normal air through lime-water produces a similar effect. A bottle containing lime-water soon becomes coated with carbonate of calcium from absorption of atmospheric carbonic acid gas.

4. Fill a dry test-tube with the gas by pressing the delivery-tube of the above apparatus to the bottom of the test-tube. Being rather more than once and a half as heavy as the air (1.529), it will displace the latter. Prove the presence of the gas by pouring it slowly, as if a visible liquid, into another test-tube containing lime-water; the characteristic cloudiness and precipitate are obtained on gently shaking the lime-water.

In testing for carbonates by bringing evolved gas into contact with lime-water, the preparation and adaptation of a delivery-tube may often be avoided by pouring the gas from the generating-tube into that containing the lime-water in the manner just indicated.

5. Pass carbonic acid gas through lime-water until the precipitate at first formed is dissolved. The resulting liquid is a

solution of carbonate of calcium in carbonic acid water. Boil the solution; carbonic acid gas escapes, and the carbonate is again precipitated.

This experiment will serve to show how chalk is kept in solution in ordinary well-waters, giving the property of "hardness," and how the *fur* or stone-like deposit in tea-kettles and boilers is formed. It should be here stated that sulphate of calcium produces similar hardness, and that these, with small quantities of the sulphate and carbonate of magnesium, constitute the hardening constituents of well-waters, a curd (oleate of calcium or magnesium) being formed whenever soap is used with such waters. An enormous amount of soap is wasted through the employment of hard water for washing purposes. The hardness produced by the earthy carbonates is termed "temporary hardness," because removable by ebullition; that by the earthy sulphates "permanent hardness," because unaffected by ebullition. The addition of lime-water or a mixture of lime and water removes temporary hardness (reac. 2, page 311) and carbonate of sodium, "washing soda," both temporary and permanent hardness, in the latter case sulphate of sodium remaining in solution. Carbonate of barium (ground witherite) also decomposes sulphates of calcium and magnesium, sulphate of barium being precipitated and carbonates of calcium or magnesium formed; the latter and the carbonates originally in the water may then be precipitated by ebullition or by the action of lime-water. But the injurious effects of barium salts on man and the lower animals prevent the carbonate being used for purifying water for drinking purposes, as by accident or an unforeseen reaction a portion might become dissolved.

QUESTIONS AND EXERCISES.

525. Name the chief natural carbonates.

526. What are the formulæ of carbonic acid and carbonic acid gas?

527. Adduce evidence of the existence of true carbonic acid.

528. Trace the steps by which the carbonic constituent of chalk is transferred to sodium by the process usually adopted in alkali-works—the manufacture of "soda."

529. Carbonic acid gas is constantly exhaled from the lungs of animals; why does it not accumulate in the atmosphere?

530. What is the effect of pressure on carbonic acid gas?

531. State the specific gravity of carbonic acid gas.

532. By what processes may carbonic acid gas be obtained for experimental and manufacturing purposes?

533. Describe the action of carbonic acid gas on the carbonates of potassium or sodium.

534. How may carbonic acid be detected in expired air?

535. To what extent is carbonic acid gas heavier than air?

536. Work sums showing what quantity of chalk (90 per cent.

pure) will be required to furnish the carbonic acid necessary to convert one ton of carbonate of potassium (containing 83 per cent. of K_2CO_3) into acid carbonate, supposing no gas to be wasted?—*Ans.* 1500 lbs.

537. Define "hardness" in water.

538. How may the presence of carbonates be demonstrated?

OXALIC ACID AND OTHER OXALATES.

Formula of Oxalic Acid $H_2C_2O_4,2H_2O$. Molecular weight 126.

Source.—Oxalates occur in nature in the juices of some plants, as wood-sorrel, rhubarb, the common dock, and certain lichens; but the hydrogen oxalate (oxalic acid) and other oxalates are all made artificially. The carbon of many organic substances yields oxalic acid when those substances are boiled with nitric acid, and an alkaline oxalate when they are roasted with a mixture of the hydrates of potassium and sodium.

Experimental Process.—On the small scale, a mixture of nitric acid 10 parts, loaf sugar 2 parts, and water 3 parts, quickly yields the acid. Abundance of red fumes are at first evolved. On cooling, crystals are deposited. A more dilute acid, kept warm, acts more slowly, but yields a larger product.

Manufacturing Process.—On the large scale, sawdust is roasted with alkalies, resulting oxalate of sodium decomposed by lime with formation of oxalate of calcium, the latter digested with sulphuric acid, and the liberated oxalic acid (Oxalic Acid of Commerce, B. P.) made commercially pure by recrystallization (Oxalic Acid Purified, B. P.).

Chemically pure Oxalic Acid.—The acid made from sugar, recrystallized two or three times, is quite pure. Commercial acid should be mixed with insufficient water for complete solution, and the mixture occasionally shaken. Impurities remain undissolved, and the saturated solution evaporated yields crystals which seldom require to be recrystallized.

Quantivalence.—The elements represented by the formula C_2O_4 are those characteristic of oxalates. They form a bivalent grouping; hence normal oxalates ($R'_2C_2O_4$) and acid oxalates ($R'HC_2O_4$) exist.

Salt of sorrel is a crystalline compound of oxalic acid with acid potassium oxalate, the crystals containing two molecules of water of crystallization ($KHC_2O_4,H_2C_2O_4,2H_2O$).

Oxalate of iron (*Ferri Oxalas*, U. S. P., FeC_2O_4,H_2O) is a crystalline yellow powder. It may be made by precipitating a solution of sulphate of iron with an oxalate. When heated in contact with air it decomposes with a faint combustion, and leaves a residue of not less than 49.3 per cent. of red oxide of iron.

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of an oxalate (oxalate of ammonium, *e. g.*) add solution of chloride of calcium; a white precipitate falls. Add to the precipitate excess of acetic acid; it is insoluble. Add hydrochloric acid; the precipitate is dissolved.

The formation of a white precipitate on adding a calcium or barium salt, insoluble in acetic but soluble in hydrochloric or nitric acid, is usually sufficient proof of the presence of an oxalate. The action of the liquid on litmus-paper, effervescence with carbonate of sodium, and absence of metals, would indicate that the oxalate is that of hydrogen, oxalic acid.

Note—The *barium* oxalate *is* slightly soluble in acetic acid (Souchay and Lenssen), and enough may be dissolved by this acid from a mixed barium precipitate (produced on adding chloride or nitrate of barium to a solution of mixed salts) to give the foregoing reaction on adding chloride of calcium to the filtered acetic liquid—an effect sometimes useful in the analysis of mixed substances (Davies).

Antidote.—In cases of poisoning by oxalic acid or salt of sorrel, chalk and water may be administered as a chemical antidote (with the view of producing the insoluble oxalate of calcium), emetics and the stomach-pump being used as soon as possible.

Second Analytical Reaction.—Heat a fragment of any dry common fixed metallic oxalate (an oxalate of potassium, for example) in a test-tube; decomposition occurs, carbonic oxide (CO) (a gas that will be noticed subsequently) is liberated, and a carbonate of the metal remains. Add water and then an acid to the residue; effervescence occurs.

This is a ready test for ordinary insoluble oxalates, and is trustworthy if, on heating the substance, no charring occurs, or not more than gives a gray color to the residue. Organic salts of metals decompose when heated, and leave a residue of carbonate, but except in the case of oxalate the residue is always accompanied by much charcoal. Insoluble oxalates and organic salts of such metals as lead and silver are, of course, liable to be reduced to oxide or even metal by heat. Such oxalates may be decomposed by boiling with solution of carbonate of sodium, filtering, and testing the filtrate for oxalates by the chloride-of-calcium test.

Other Analytical Reactions.—Nitrate of silver gives, with oxalates, white oxalate of silver ($Ag_2C_2O_4$).——Dry oxalates are decomposed when heated with strong sulphuric acid, carbonic oxide and carbonic acid gas escaping. If much of the substance be operated on, the gas may be washed with an alkali, the carbonic acid be thus removed, and the carbonic oxide be ignited; it will be found to burn with a characteristic bluish flame.——Oxalates, when mixed with water, black oxide of manganese (free from carbonates), and sulphuric acid, yield carbonic acid gas, which may be tested by lime-water in the usual manner.——Not only such insoluble oxalates as those of lead and silver, above referred, to, but any common insoluble oxalates, such as those of calcium and magnesium, may be decomposed by ebullition with solution of carbonate of sodium; after filtration the oxalic radical will be found in the clear liquid as soluble oxalate of sodium.

Test of Purity.—"Purified oxalic acid . . . . is entirely dissipated by a heat below 350° F." (B. P.).

QUESTIONS AND EXERCISES.

539. Explain the constitution of oxalates.
540. State how oxalates are obtained.
541. What is the quantivalence of the oxalic radical?
542. Give the formula of "salt of sorrel."
543. Mention the chief test for oxalic acid and other soluble oxalates.
544. Name the antidote for oxalic acid, and describe its action.
545. By what reactions are insoluble oxalates recognized?

TARTARIC ACID AND OTHER TARTRATES.

Formula of Tartaric Acid $H_2C_4H_4O_6$, or $H_2\overline{T}$.
Molecular weight 150.

Source.—Tartrates exist in the juice of many fruits; but it is from that of the grape that our supplies are usually obtained. Grape-juice contains much acid tartrate of potassium ($KHC_4H_4O_6$), which is gradually deposited when the juice is fermented, as in making wine; for acid tartrate of potassium, not very soluble in aqueous liquids, is still less so in spirituous, and hence crystallizes out as the sugar of the grape-juice is gradually converted into alcohol. It is found with tartrate of calcium lining the vessels in which wine is kept; and it is from this crude substance, termed *argal* or *argol*, also from the albumenoid yeasty matter or "lees" deposited at the same time, as well as from what tartrate may be remaining in the marc left after the juice has been pressed from the grapes, that by rough crystallization "tartar," still containing 6 or 7 per cent. or more of tartrate of calcium ($CaC_4H_4O_6,4H_2O$), is obtained. From the latter tartaric acid and other tartrates are prepared. In old dried grapes (Raisins; *uvæ*, B. P.) crystalline masses of tartar and of grape-sugar are constantly met with.

Cream of Tartar, purified by crystallization (*Potassii Bitartras*, U. S. P.), occurs as a "gritty white powder, or fragments of cakes crystallized on one surface;" of a pleasant acid taste, soluble in 180 parts of cold and 6 of boiling water, insoluble in spirit.* "If 1 gm. of Bitartrate of Potassium be digested with 5 c.c. of diluted acetic acid for half an hour, then diluted with distilled water to 500 c.c., the solution agitated and filtered, and 25 c.c. of the filtrate treated with 5 c.c. of test-solution of oxalate of ammonium, the liquid should not become cloudy in less than one minute, nor distinctly turbid in less than one minute and a half (absence of more than 6 per cent. of tartrate of calcium)."—U. S. P.

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* A boiling solution of tartar yields a floating crust of minute crys-

Quantivalence.—The elements represented by the formula $C_4H_4O_6$ are those characteristic of tartrates. They form a bivalent grouping; hence normal tartrates ($R'_2\overline{T}$) and acid tartrates ($R'H\overline{T}$) exist. Tartrate of potassium, the *Potassii Tartras* of the U. S. Pharmacopœia ($K_2C_4H_4O_6$), and Rochelle Salt, or tartrate of potassium and sodium ($KNaC_4H_4O_6,4H_2O$), the official *Potassii et Sodii Tartras* (*Soda Tartarata*, B. P.), are illustrations of normal tartrates, while Cream of Tartar is an example of acid tartrates. The only official tartrate not apparently included in these general formulæ is tartar-emetic (*Antimonium Tartaratum*, B. P., *Antimonii et Potassii Tartras*, U. S. P.), which is sometimes regarded as the double tartrate of potassium and a hypothetical radical, antimonyl (SbO), thus, $KSbOC_4H_4O_6$. Probably, however, it is but an oxytartrate of antimony ($Sb_2O_2\overline{T}$) with normal tartrate of potassium ($K_2\overline{T}$); for there are several oxycompounds of antimony analogous to the oxycompounds of bismuth that have been described (p. 249), normal salts partially decomposed by water into oxides, and many of these oxycompounds readily unite with normal salts of other basylous radicals. Tartar-emetic would thus be oxytartrate of antimony, with tartrate of potassium ($Sb_2O_2\overline{T},K_2\overline{T}$, or $Sb_2O_2C_4H_4O_6,K_2C_4H_4O_6$).

Tartaric Acid.

Tartaric Acid (*Acidum Tartaricum*, U. S. P.) is obtained by boiling cream of tartar (*Potassii Bitartras*, U. S. P.) with water, adding chalk till effervescence ceases, and then chloride of calcium so long as a precipitate falls; the two portions of tartrate of calcium thus consecutively formed are thoroughly washed, treated with sulphuric acid, the mixture boiled for a short time, resulting sulphate of calcium mostly separated by filtration, the filtrate concentrated by evaporation, any sulphate of calcium that may have deposited removed as before, and concentration continued until the solution is strong enough to crystallize. Tartrate of calcium from 9 ounces of cream of tartar requires 5 ounces by weight of sulphuric acid for complete decomposition.

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tals on cooling—just as milk yields a floating layer of cream, hence the term *cream* of tartar.

"It is called *tartar*," says Paracelsus, "because it produces oil, water, tincture, and salt, which burn the patient as Tartarus does." *Tartarus* is Latin (Τάρταρος, Tartaros, Greek) for *hell*. The products of its destructive distillation are certainly somewhat irritating in taste and smell; and the "salt" (carbonate of potassium) that is left is diuretic, and, in larger quantities, powerfully corrosive.

$$\underset{\text{Acid tartrate of potassium.}}{2KHT} + \underset{\text{Carbonate of calcium.}}{CaCO_3} = \underset{\text{Tartrate of calcium.}}{Ca\bar{T}} + \underset{\text{Tartrate of potassium.}}{K_2\bar{T}} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

$$\underset{\text{Tartrate of potassium.}}{K_2\bar{T}} + \underset{\text{Chloride of calcium.}}{CaCl_2} = \underset{\text{Tartrate of calcium.}}{Ca\bar{T}} + \underset{\text{Chloride of potassium.}}{2KCl}$$

$$\underset{\text{Tartrate of calcium.}}{2Ca\bar{T}} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Sulphate of calcium.}}{2CaSO_4} + \underset{\text{Tartaric acid.}}{2H_2\bar{T}}$$

Tartaric acid occurs in trade in colorless crystals, or the same powdered. It is strongly acid and readily soluble in water or spirit. One part in 8 of water and 2 of spirit of wine forms "Solution of Tartaric Acid," B. P. Its aqueous solution is not stable.

Parcels of tartaric acid often contain crystals of an allotropic or physically isomeric modification (*vide* "Allotropy" and "Isomerism" in Index). It is termed *Paratartaric acid* (παρὰ, *para*, beside) or *Racemic acid* (*racemus*, a bunch of grapes), and is a combination of ordinary tartaric acid, whose solution twists a ray of polarized light to the right hand (dextrotartaric or dextroracemic acid), and of lævotartaric or lævoracemic acid, whose solution twists a polarized ray to the left. Racemic acid is inactive in this respect, the opposite properties of its constituents neutralizing each other. Racemic acid is less soluble in alcohol than tartaric acid.

REACTIONS.

Tartrate of Potassium.

Synthetical Reaction.—To a small quantity of a strong solution of carbonate of potassium add acid tartrate of potassium so long as effervescence occurs; the resulting liquid is solution of normal tartrate of potassium (*Potassii Tartras*, U. S. P.) ($K_2\bar{T}$), crystals of which may be obtained on evaporation.

Note.—This is a common method of converting an acid salt of a bivalent acidulous radical into a normal salt. The carbonate added need not be a carbonate of the same, but may be of a different metal; compounds like Rochelle salt ($KNa\bar{T}$) are then obtained. Thus:—

Tartrate of Potassium and Sodium.

To a strong hot solution of carbonate of sodium add acid tartrate of potassium until effervescence ceases; the resulting liquid is solution of tartrate of potassium and sodium; on cooling, it yields crystals. This is the official process (*Soda Tartarata*, B. P.; *Potassii et Sodii Tartras*, U. S. P.) ($KNaC_4H_4O_6,4H_2O$).

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} = \underset{\text{Tartrate of potassium and sodium.}}{2KNaC_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Crystals of Rochelle salt are usually halves of colorless, transparent, right rhombic prisms, slightly efflorescent in dry air, soluble in five parts of boiling water. Tartrate of potassium is slightly deliquescent, soluble in about four parts of boiling water.

Equivalent Weights *of Tartaric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium, Bicarbonate of Sodium, and Carbonates of Ammonium and Magnesium; repeated for 20 parts of each* (and, incidentally, for other proportions).

Tart. Acid............	$H_2C_4H_4O_6$.................... = 150	20	18¼	15	10½	17¾	25½	31½
Carb. Potas............	K_2CO_3 (of 84 per cent.).. = 164	22	20	16½	11½	19½	28	34½
Bicarb. Pot...........	$2(KHCO_3)$..................... = 200	26¾	24¼	20	14	3¾	34	42
Carb. Soda (cryst.).	$Na_2CO_3,10H_2O$ .... = 286	38	24¾	28½	20	34	48½	60
Bicarb. Soda.........	$2(NaHCO_3)$.................... = 168	22½	20	16¾	11¾	20	28½	35¼
Carb. Ammon.........	$(N_4H_{16}C_3O_8)\div 2$ .... = 118	15¾	14¼	11¾	8¼	14	20	24¾
Carb. Magnes........	$(MgCO_3)_3Mg2HO,4H_2O$.. = 95.5	12¾	11½	9¾	6¾	11¼	16	20

Thus 20 parts (grains or other weights) of tartaric acid neutralize 22 of carbonate of potassium, 26¾ of bicarbonate of potassium, 38 of carbonate of sodium, 22½ of bicarbonate of sodium, 15¾ of carbonate of ammonium, or 12¾ of carbonate of magnesium. Other quantities of tartaric acid (18¼, 15, 10½, 16¾, 25½, 31½) saturate the amounts of salts mentioned in the other columns, and *vice versâ*. A similar Table for Citric Acid will be found on page 322, and for both acids in the Appendix. These Tables afford good illustrations of the laws of chemical combination (page 47). The reader should verify a few of the numbers by calculation from the atomic weights of the elements concerned in the reactions, remembering that the salts formed are considered to be neutral in constitution. In medical practice effervescing saline draughts are often designedly prescribed to contain an amount of acid or alkali considerably in excess of the proportions required for perfect neutrality.

A common form of *Seidlitz Powder* consists of 3 parts of Rochelle salt (120 grains) with 1 (40 grains) of acid carbonate of sodium (the mixture usually wrapped in blue paper), and 1 (40 grains) of tartaric acid (wrapped in white paper). When administered, the latter is dissolved in a tumbler rather more than half full of water, the former added, and the mixture drank during effervescence. It will be seen that the salts swallowed are tartrate of potassium and sodium ($KNa\overline{T},4H_2O$), tartrate of sodium ($Na_2\overline{T},2H_2O$), and acid tartrate of sodium or of potassium. The last-mentioned salt results because (for one reason) 11¼ per cent. (4½ grains) of the tartaric acid is in excess of the quantity necessary for the formation of neutral tartrate of sodium. This amount of acid salt gives agreeable acidity to the draught. The United States formula (*Pulvis Effervescens Compositus*, U. S. P.) includes rather less tartaric acid, so that only neutral salts are formed,

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of any normal tartrate, or tartaric acid made neutral by solution of soda, add solution of chloride of calcium; a white precipitate, tartrate of calcium, falls. Collect the precipitate on a filter, wash, place a small quantity in a test-tube, and add solution of potash; on stirring the mixture the precipitate dissolves. Heat the solution; the tartrate of calcium is again precipitated.

In the above reaction a fair amount of the chloride of calcium solution should be added at once, and the whole test performed without delay, or the calcium tartrate will assume a crystalline character, and be with difficulty dissolved by the potash.

The solubility of tartrate of calcium in cold potash solution enables the analyst to distinguish between tartrates and citrates, otherwise a difficult matter. Citrate of calcium is not soluble, or only to a very slight extent, in the alkali. The absence of much ammoniacal salt must be insured, citrate as well as tartrate of calcium being soluble in solutions of salts of ammonium.

Second Analytical Reaction.—Acidulate a solution of a tartrate with acetic acid, add acetate of potassium, and well stir the mixture; a crystalline precipitate of acid tartrate of potassium slowly separates.

This reaction is not applicable in testing for very small quantities of tartrates, the acid tartrate of potassium being not altogether insoluble. The precipitate being insoluble in alcohol, however, the addition of spirit of wine renders the test far more delicate. One part of acid should yield 1¼ of salt.

Third Analytical Reaction.—To a neutral solution of a tartrate add solution of nitrate of silver; a white precipitate of tartrate of silver, $Ag_2C_4H_4O_6$, falls. Boil the mixture; it blackens, owing to the reduction of the salt to metallic silver. Or, before boiling, add a drop, or less, of ammonia; a mirror will form on the tube—adhering well to the glass if the tube was thoroughly cleansed. Even an insoluble tartrate, placed in a dry tube with a few fragments of nitrate of silver and a drop, or less, of ammonia added, gives a mirror-like character to each fragment of the silver salt when the tube is gently rotated some inches above a flame.

Fourth Analytical Reaction.—To a neutral or alkaline solution of a tartrate add a few drops of solution of permanganate of potassium, and slowly heat the test-tube; the color is discharged, an oxide of manganese being precipitated. Citrates only reduce the permanganate to green manganate.

Other Reactions.—Tartrates heated with strong sulphuric acid char immediately.——Tartaric acid and the soluble tartrates prevent the precipitation of ferric and other hydrates by alkalies, soluble double tartrates being formed (which on evaporation yield liquids that do not crystallize, but, spread on sheets of glass, dry up to thin transparent plates or scales). The *Ferri et Potassii Tartras*, U. S. P. (*Ferrum Tartaratum*, B. P.), is a preparation of this kind.——Tartrates decompose when heated, carbonates being formed and carbon set free, the gaseous products having a peculiar, more or less characteristic smell, resembling that of burnt sugar.

QUESTIONS AND EXERCISES.

546. State the origin of tartaric acid and other tartrates, and explain the deposition of argol, crude acid tartrate of potassium, during the manufacture of wine.

547. What is the chemical formula and what are the characters of "cream of tartar"?

548. Mention the formula and quantivalence of the tartaric radical.

549. Write formulæ of normal, acid, and double tartrates, tartar-emetic being treated as an oxytartrate of antimony with tartrate of potassium.

550. Give equations or diagrams illustrative of the production of tartaric acid from cream of tartar.

551. By what general process may normal or double tartrates be obtained from acid tartrate of potassium?

552. Work out sums proving the correctness of some of the figures given on p. 318 as showing the saturating power of tartaric acid for various quantities of different carbonates, and give diagrams or equations of the reactions.

553. State the names and work sums showing the quantities of the salts resulting from the admixture of 120 grains of tartrate of potassium and sodium, 40 grains of acid carbonate of sodium, and 40 grains of tartaric acid (Seidlitz powder).

554. Enumerate the tests for tartrates, and explain the effects of heat on tartrates of the metals.

CITRIC ACID AND OTHER CITRATES.

Formula of Citric Acid $H_3C_6H_5O_7,H_2O$ or H_3CiAq.
Molecular weight 210.

Source.—Citric acid (*Acidum Citricum*, U. S. P.) exists in the juice of the gooseberry, currant, cherry, strawberry, raspberry (*Rubus*, U. S. P.) and many other fruits, and in other parts of plants. The pulp of the fruit of *Tamarindus indica* (*Tamarindus*, U. S. P.) contains from 1 to 12 per cent. (in addition to 1.5 of tartaric acid, 5 of malic acid, and 3 per cent. of acid tartrate of potassium). But it is from the lemon or lime that the acid of commerce is usually obtained. For this purpose concentrated lemon-juice is exported from Sicily, concentrated bergamot juice from the Calabrian coast of South Italy, and concentrated lime-juice from the West Indies. The lime-fruit from *Citrus bergamia* is official in the Pharmacopœia of India.

Process.—The British Pharmacopœia directs that the hot lemon-juice (4 pints) be saturated by powdered chalk, that is, whiting (4½ ounces), the resulting citrate of calcium collected on a filter, washed with hot water till the liquor passes from it colorless (by which not only the coloring-matter, but the mucilage, sugar, and other constituents of the juice are got rid of), then mixed with cold water (1 pint) decomposed by sulphuric acid (2½ fluidounces in 1½ pints of water), the mixture boiled for half an hour, filtered, the solution evaporated to a density of 1.21, set aside for 24 hours, then poured off from any deposit of crystalline sulphate of calcium, further concentrated, and set aside to crystallize. If the quantity of citrate of calcium to be decomposed is indefinite, the sulphuric acid may be added until a little of the supernatant fluid gives, after a minute or two, a precipitate with solution of chloride of calcium. The concentrated citric solution generally crystallizes very slowly. Shaken violently, however, in a bottle, with a granule or two of solid acid, it quickly yields its citric acid in a pulverulent form, and this, drained and redissolved in a very small quantity of hot water, yields crystals fairly quickly (Warington).

$$\underset{\substack{\text{Citric acid}\\\text{(impure).}}}{2H_3C_6H_5O_7} + \underset{\substack{\text{Carbonate of}\\\text{calcium.}}}{3CaCO_3} = \underset{\substack{\text{Citrate of}\\\text{calcium.}}}{Ca_32C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

$$\underset{\substack{\text{Citrate of}\\\text{calcium.}}}{Ca_32C_6H_5O_7} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Citric acid}\\\text{(pure).}}}{2H_3C_6H_5O_7} + \underset{\substack{\text{Sulphate of}\\\text{calcium.}}}{3CaSO_4}$$

Quantivalence.—The elements represented by the formula $C_6H_5O_7$ are those characteristic of citrates. They form a trivalent grouping; hence three classes of salts may exist—one, two, or three atoms of the basylous hydrogen in the acid, $H_3C_6H_5O_7$, being displaced by equivalent proportions of other basylous radicals.

Citric acid itself is the only citric compound of much direct importance to the pharmacist. It usually occurs in colorless crystals soluble in half their weight of boiling and three-fourths of cold water, less soluble in spirit, and insoluble in ether. A solution of about 34 grains in 1 ounce of water forms a sort of artificial lemon-juice. Citrates heated with strong sulphuric acid to about 212° F. evolve carbonic oxide gas, and at higher temperatures acetone and carbonic acid gas.

The artificial production of citric acid has been accomplished by Grimaux and Adam, who starting with glycerin, produce certain chloro- and cyano-derivatives, and ultimately citric acid itself.

Action of Heat on Citric Acid.—Citric acid slowly heated first loses its water of crystallization; afterwards (at 347° F.) the elements of another molecule of water are evolved and a residue obtained from which ether extracts *aconitic acid* ($H_3C_6H_3O_6$), identical with the aconitic acid (and the acid first termed *equisetic*) in various species of *Aconitum* and *Equisetum*.

The official Lemon Juice (*Limonis Succus*, U. S. P.) is to be freshly expressed from the ripe fruit, and to contain about 7 per cent. of citric acid. *Lime Juice* contains an average of 7.84 per cent. of citric acid, rarely rising to 10 per cent., and very seldom falling to 7 per cent. Containing but little sugar and mucilage, it requires no addition of spirit to preserve it. Lemon juice requires about 40 per cent. of proof spirit to prevent fermentation (Conroy). The acidity may be ascertained by adding solution of potash or soda (the strength of which has been previously determined with pure crystals of citric acid) till red litmus-paper is fairly turned blue. Before applying this test to commercial specimens, the absence of notable quantities of sulphuric, hydrochloric, acetic, tartaric, or other acid must be insured by application of appropriate reagents. (See also "Lemon Juice," in Index.)

Mistura Potassii Citratis, U. S. P., is lemon-juice completely neutralized by bicarbonate of potassium. It is a slightly impure but flavored solution of citrate of potassium.

Equivalent Weights *of Citric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium, Bicarbonate of Sodium, and Carbonates of Ammonium and Magnesium; repeated for 20 parts of each* (and, incidentally, for other proportions.)

Citric Acid............	$H_3C_6H_5O_7,H_2O$............ = 210	20	17	14	9¾	16¾	23¾	29¼
Carb. Potas.	(K_2CO_3, of 84 p. ct.) ÷ 2 × 3 = 246½	23½	20	16⅓	11½	19⅔	28	34¼
Bicarb. Pot...........	3($KHCO_3$)...................... = 300	28½	24¼	20	14	24	34	41¾
Carb. Sod. (cryst.)..	($Na_2CO_3,10H_2O$) ÷ 2 × 3.. = 429	40	34¾	28½	20	34¼	48½	60
Bicarb. Sod...........	3($NaHCO_3$)...................... = 252	24	20½	16¾	11¾	20	28½	35
Carb. Ammon........	($N_4H_{16}C_3O_8$) ÷ 4 × 3...... = 177	16¾	14¼	11¾	8¼	14	20	24¾
Carb. Magnes.......	$(MgCO_3)_3Mg2HO,4H_2O$ ÷ 8 × 3 = 143¼	13½	11¾	9½	6¾	11½	16¼	20

Thus 20 parts (grains or other weights) of citric acid neutralize 23½ of carbonate of potassium, 28½ of bicarbonate of potassium, 40 of carbonate of sodium, 24 of bicarbonate of sodium, 16¾ of carbonate of ammonium, or 13½ of carb. of magnesium. Other quantities of acid (17, 14, 9¾, 16¾, 23¾ 29¼) saturate the amount of salts mentioned in the other columns, and *vice versâ*.

This Table, the similar one for tartaric acid (p. 318), and that for both acids (*vide* Appendix) afford good illustrations of some of the laws of chemical combination (p. 47). The reader should verify a few of the numbers by calculation from the atomic weights of the elements concerned in the reactions, remembering that the salts formed are considered to be neutral in constitution. In medical practice, effervescing saline draughts are often designedly prescribed to contain an amount of acid or alkali considerably in excess of the proportions required for perfect neutrality.

Analytical Reactions (*Tests*).

First Analytical Reaction.—To a dilute solution of any neutral citrate, or citric acid carefully neutralized by alkali, add solution of chloride of calcium and boil; a white precipitate, citrate of calcium ($Ca_3\overline{Ci}_2$), falls. Treat the precipitate, as for tartrate of calcium (p. 319); it is not perceptibly dissolved by the potash.

A mixture of citrates and tartrates can be separated by this reaction. They are precipitated as calcium salts, and the rapidly washed precipitate mixed with solution of potash, diluted, and filtered; the filtrate contains the tartrate, which is shown to be present by reprecipitation on boiling. The precipitate still on the filter is washed, dissolved in solution of chloride of ammonium, and the solution boiled; the citrate of calcium is reprecipitated. The presence of much sugar interferes with this reaction. A dilute solution of a citrate is not precipitated by chloride of calcium until the liquid is heated; precipitation from a strong solution, also, is not thoroughly complete without ebullition of the mixture. This reaction is not thoroughly satisfactory, citrate of calcium being *slightly* soluble in alkalies, in the solutions of salts produced in the reaction, and, to a very slight extent, even in cold water.

Second Analytical Reaction.—To a neutral solution of a citrate add solution of nitrate of silver; a white precipitate of citrate of silver ($Ag_3\overline{Ci}$) falls. Boil the mixture; the precipitate does not turn black as a tartrate of silver does, or only after long boiling.

Third Analytical Reaction.—To a neutral or alkaline solution of a citrate add a few drops of solution of permanganate of potassium and slowly heat the test-tube; reduction to manganate only occurs, a green or reddish-green solution resulting. Tartrates reduce the permanganate entirely.

Other Analytical Reactions—Citric acid forms no precipitate corresponding with the acid tartrate of potassium.——Lime-water, in excess, gives no precipitate with citric acid or citrates, unless the solution is boiled, citrate of calcium being slightly soluble in cold but not in hot water; it usually precipitates tartrates in the cold.——Citrates, when heated with strong sulphuric acid, do not char immediately.——Citric acid and citrates prevent the precipitation of oxide of iron by alkalies, soluble double compounds being formed. The *Ferri et Ammonii Citras*, U. S. P., is a preparation of this kind.——Metallic citrates decompose when heated, carbonates being formed and carbon set free: the odor of the gaseous products is not so characteristic as that of tartrates.——According to Cailletet, a cold saturated solution of red chromate of potassium turns a solution of tartaric acid dark brown, carbonic acid gas being evolved, while a solution of citric acid only slowly becomes of a light brown.

QUESTIONS AND EXERCISES.

555. What is the source of citric acid?

556. Describe the method by which citric acid is prepared, giving diagrams.

557. Illustrate by formulæ the various classes of tartrates and citrates.

558. State the average proportion of citric acid in lemon-juice.

559. Work out the sums proving the correctness of some of the figures given on page 322 as showing the saturating-power of citric acid for various carbonates.

560. What are the tests for citrates?

561. How are the tartrates separated from citrates?

PHOSPHORIC ACID AND OTHER PHOSPHATES.

Formula of Phosphoric Acid H_3PO_4. Molecular weight 98.

Source.—The source of the ordinary normal phosphates and of phosphorus itself (*Phosphorus*, U. S. P.) is the normal phosphate of calcium (Ca_32PO_4). It is the chief constituent of the bones of animals, being derived from the plants on which they feed, plants again obtaining it from the soil. Compounds of phosphorus are also met with in the brain, nerves, muscles, blood, saliva, and, according to Kirkes, even in tissues so simple that one must assume that the compounds are necessary constituents of the substance of the primary cell. They escape from the system both in the urine and in the fæces.

Process.—Phosphorus (P = 31) is obtained from bones by the following processes: The bones are burnt to remove all traces of animal matter. The resulting *bone-earth* is treated with sulphuric acid and water, by which an acid phosphate of calcium (CaH_42PO_4), often called *superphosphate of lime*, is produced:—

$$Ca_32PO_4 + 2H_2SO_4 = CaH_42PO_4 + 2CaSO_4.$$

The acid phosphate (strained from the sulphate and evaporated to dryness) is mixed with charcoal and sand, and heated to dull redness in an iron pot. At this stage water escapes and metaphosphate of calcium ($Ca2PO_3$, see Index) remains:—

$$CaH_42PO_4 = Ca2PO_3 + 2H_2O.$$

The mixture is then transferred to a retort, and distilled at a strong red heat; a silicate of calcium ($CaSiO_3$) is formed and remains in the retort, phosphorus vapor is evolved and condensed under water, and carbonic oxide gas escapes:—

$$2(Ca2PO_3) + 2SiO_2 + C_{10} = 2CaSiO_3 + 10CO + P_4.$$

It is purified by melting under water containing sulphuric acid and red chromate of potassium.

Properties.—Phosphorus is a "semi-transparent, colorless, wax-like solid (in sticks or cakes), which emits white vapors when exposed to the air. Specific gravity 1. 77. It is soft and flexible at common temperatures, melts at 110° F., ignites in the air at a temperature a little above its melting-point, burning with a luminous flame and producing dense white fumes. It is very poisonous. Insoluble in water, but soluble in ether and in boiling oil of turpentine," also in bisulphide of carbon. It is soluble in oil which has been previously heated for a short time to about 482° F. to expel moisture: 1 part in 90 parts of dried almond oil with 9 parts of ether constituting Phosphorated Oil, *Oleum Phosphoratum*, U. S. P. A mixture, or rather a solution, of phosphorus in chloroform, mixed with althea, acacia, and glycerin, forms the official Phosphorus Pills (*Pilulæ Phosphori*, U. S. P.).

Granulated or pulverulent phosphorus is obtained by placing a portion under equal parts of spirit and water in a bottle, standing the bottle in warm water till the phosphorus melts, then inserting the stopper (glass, not cork), and shaking the whole till cold.

Red or Amorphous Phosphorus.—Ordinary phosphorus kept at a temperature of about 450° F., in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500° F. It is used in the manufacture of several varieties of lucifer matches, not emitting the poisonous, jaw-destroying fumes given by ordinary phosphorus.

Quantivalence.—The atom of phosphorus is quinquivalent, as seen in the pentachloride (PCl_5) and oxychloride (PCl_3O); but it often exhibits trivalent activity, as seen in the trichloride (PCl_3) and trihydride (PH_3).

Phosphide of Zinc, Zn_3P_2 (*Zinci Phosphidum*, U. S. P.), occurs as a grayish-black powder or in crystalline fragments having a metallic lustre. It may be obtained by throwing phosphorus upon melted zinc.

Molecular Weight.—Phosphorus is an exception to the rule that the atomic weights (in grains, grammes, etc.) of elements occupy similar volumes of vapor at similar temperatures, the equivalent weight of phosphorus (31) only giving half such a volume. Hence while the molecular weights, that is, double the atomic weights, of oxygen ($O_2 = 32$), hydrogen ($H_2 = 2$), nitrogen ($N_2 = 28$), etc., give a similar bulk of vapor at any given temperature, the double atomic weight of phosphorus ($P_2 = 62$) only gives half this bulk; that is, four times the atomic weight of phosphorus must be taken to obtain the whole bulk. It would appear therefore that the molecule of phosphorus contains four atoms ($P_4 = 124$). As with sulphur, however, phosphorus in the state ordinarily known to us may be abnormal, and a variety yet be found in which the molecular weight is double the atomic weight.

Phosphoric Acid.

The chief use of phosphorus in pharmacy is the formation of Diluted Phosphoric Acid. Phosphorus is boiled with nitric acid and water until dissolved. The solution, evaporated to a low bulk to remove nitrous compounds, and rediluted so as to contain 50 per cent. of acid (H_3PO_4), constitutes the *Acidum Phosphoricum*, U. S. P., a colorless liquid of specific gravity 1.347. If the necessary appliances are at hand, an ounce or two of this acid may be prepared by the official process as follows: Boil together, in a retort attached to a Liebig's condenser, 160 grains of phosphorus, 1000 grains of the official nitric acid, and 1000 grains of water. When about 1 oz. of water has distilled over, it should be returned to the retort, and the operation repeated until the phosphorus has disappeared.

$$\underset{\text{Phosphorus.}}{3P_4} + \underset{\text{Nitric acid.}}{20HNO_3} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Phosphoric acid.}}{12H_3PO_4} + \underset{\text{Nitric oxide.}}{20NO}$$

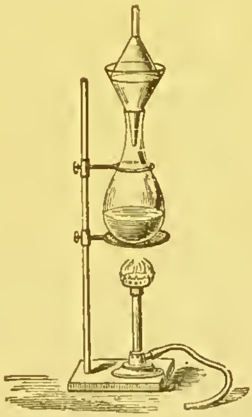
The liquid remaining in the retort is then transferred to a dish (preferably of platinum), evaporated down to about half an ounce, and, lastly, diluted with distilled water until the product weighs 1000 grains.

One part, by weight, of the official phosphoric acid with four of water yields *Acidum Phosphoricum Dilutum*, U. S. P. It contains 10 per cent. of H_3PO_4; sp. gr. 1.057.

The use of the water in this process is to moderate the reaction. Strong hot nitric acid oxidizes phosphorus with almost explosive rapidity, hence the acid must be diluted in the first instance, and be rediluted, from time to time, to prevent its becoming too strong by loss of water. Time is saved by using a strong acid, but in that case constant supervision is necessary in order that water may be added, or the temperature otherwise reduced, when the action becomes too violent. Deficiency of nitric acid must also be avoided, or some phosphorous acid (H_2PHO_3) will be formed.

Markoe, also, to economize time, modifies the process by adding, for every ounce of phosphorus, four or five grains of iodine, and, drop by drop, twenty-five or thirty drops of bromine. The iodine and bromine unite with the phosphorus with a readiness or even violence that would be explosive if not controlled by the presence of the cold fluid—further cooled, if necessary, by immersing the vessel in cold water. Iodide of phosphorus (PI_5) and bromide of phosphorus (PBr_5) are at once formed. These, in the presence of water, immediately yield hydriodic and hydrobromic acids (HI, HBr) and phosphoric acid. The nitric acid attacks the hydriodic and hydrobromic acids, forming the lower oxides of nitrogen, which escape as gas, water, and free iodine and bromine. The latter unite with more phosphorus, and the reactions are repeated. This carrying power of a little iodine or bromine, or both, would perhaps be indefinitely prolonged if no vapor of these elements or their acids escaped with the gases. The phosphorus having disappeared, excess of nitric acid is got rid of roughly by dropping in clean rags or paper (nitric oxide, carbonic acid gas, and water being formed), and the last portions by adding oxalic acid (which even still more readily yields similar products). Evaporation to a syrupy consistence finally removes all traces of iodine, bromine, oxalic acid, and moisture. The product is then diluted to any required extent.

Fig. 40.



Experimental Process.—A flask, in the neck of which a funnel is inserted, and a second funnel inverted, so that its mouth rests within the mouth of the first, is an efficient and convenient arrangement of apparatus for this process, especially if the operation be conducted slowly.

Solution of phosphoric acid evaporated to a specific gravity of 1.850 yields a mass of prismatic crystals of H_3PO_4, especially if a crystal or two be dropped into the fluid (Cooper). Further evaporated, it leaves a residue which melts at a low red heat, yielding *pyrophosphoric acid*, and, finally, *metaphosphoric acid* (*Glacial Phosphoric Acid*).

Phosphoric acid is also easily made from amorphous phosphorus (Mattison).

Prepared from bones, phosphoric acid is apt to develop fungoid deposits (Jensen). Not more than traces of arsenicum or of sulphur should be present in phosphorus, the former detected by sulphuretted hydrogen and the latter by chloride of barium solution after the phosphorus has been converted by nitric acid into phosphoric acid (U. S. P.).

Quantivalence.—The elements represented by the formula PO_4 are those characteristic of phosphates. The grouping is trivalent; hence there may exist trimetallic or normal phosphates (M'_3PO_4), dimetallic acid phosphates (M'_2HPO_4), monometallic acid phosphates ($M'H_2PO_4$), and, lastly, trihydric phosphate (H_3PO_4) or common phosphoric acid. These are the ordinary phosphates or *orthophosphates* met with in nature or used in pharmacy; the rarer pyrophosphates and metaphosphates, as well as the phosphites and hypophosphites, will be mentioned subsequently.

Analytical Reactions (Tests).

First Analytical Reaction.—To an aqueous solution of a phosphate (*e. g.* Na_2HPO_4) add solution of sulphate of magnesium with which chloride of ammonium and ammonia have been mixed; a white crystalline precipitate of ammonio-magnesium phosphate falls ($MgAmPO_4$).

Chloride of ammonium is added to prevent the precipitation of hydrate of magnesium. Arseniates, which have close analogy to phosphates, give a precipitate of similar character with the magnesium reagent.

Second Analytical Reaction.—To a neutral aqueous solution of a phosphate add solution of nitrate of silver; light-yellow phosphate of silver (Ag_3PO_4) is precipitated. To a portion of the precipitate add ammonia; it dissolves. To another portion add nitric acid; it dissolves. By this reaction phosphates may be distinguished from their close allies the arseniates, arseniate of silver being of a chocolate color.

Third Analytical Reaction.—To a solution (in a few drops of acid) of a phosphate insoluble in water (*e. g.* Ca_32PO_4) add the acetate of an alkali-metal (easily made by adding to soda or ammonia in a test-tube excess of acetic acid), and then a drop or two of solution of perchloride of iron; yellowish-white ferric phosphate (Fe_2PO_4) is precipitated, insoluble in acetic acid. Too much of the ferric chloride must not be added, or ferric acetate will be produced, in which ferric phosphate is to some extent soluble.

To remove the whole of the phosphoric radical from the solution, add ferric chloride so long as a precipitate is produced, and boil; ferric phosphate and oxyacetate are precipitated.

To obtain confirmatory evidence of the presence of phosphate in this precipitate, and to separate the phosphoric radical as a pure unmixed phosphate, collect the precipitate on a filter, wash, drop some solution of ammonia on it, then sulphydrate of ammonium, and finally wash with water; black ferrous sulphide remains on the filter, while phosphate of ammonium occurs in the filtrate. To the filtrate add a mixture of solutions of sulphate of magnesium and chloride of ammonium, and well stir; ammonio-magnesian phosphate is precipitated.

Fourth Analytical Reaction.—To diluted nitric acid add a little phosphate of calcium (or any other phosphate), and then solution of molybdate of ammonium, and gently heat; a yellow precipitate falls.

This precipitate contains what is termed phospho-molybdic acid, but is a compound of molybdic acid with phosphoric acid (about 4 per cent. of H_3PO_4) and ammonia (nearly 7 per cent.).

Molybdate of ammonium is obtained by roasting the native sulphide of molybdenum (MoS_2) to molybdic oxide or anhydride (MoO_3), dissolving the latter in water, adding ammonia, evaporating, and crystallizing.

Molybdates having the following formulæ ($M = 1$ univalent atom of any metal) have been obtained: M_2MoO_4; $MHMoO_4$; $MHMoO_4$, H_2MoO_4. According to Carrington, commercial molybdate of ammonium is commonly the intermediate of these three salts. Molybdate of sodium has the formula Na_2MoO_4,H_2O.

Note.—The foregoing two reactions are useful in the analysis of bone-earth, other earthy phosphates, phosphate of iron, and all phosphates insoluble in water. Only arseniates give similar appearances; but the acid solution of these may be decomposed by agitation with sulphurous acid and subsequent treatment with sulphuretted hydrogen, arsenious sulphide, As_2S_3, being then precipitated.

Other Analytical Reactions.—Solutions of barium and calcium salts give, with aqueous solutions of phosphates, white precipitates of the respective phosphates $BaHPO_4$, or Ba_32PO_4, and $CaHPO_4$, or Ca_32PO_4, all of which are soluble in acetic and the stronger acids.

QUESTIONS AND EXERCISES.

562. State the source of phosphorus.
563. Give equations or diagrams explanatory of the isolation of phosphorus from its natural compounds.
564. What is the composition of farmers' "superphosphate," and how is it prepared?
565. Enumerate the properties of phosphorus.
566. Mention some solvents of phosphorus.
567. How is the official Diluted Phosphoric Acid made?
568. Describe the precautions necessary to be observed in making this acid.
569. What is the strength of the official acid?
570. Write formulæ illustrative of all classes of orthophosphates.
571. Mention the chief tests for soluble and insoluble phosphates.
572. By what reactions may phosphates be distinguished from arseniates?

Vanadium, V. 51.3, is a very rare element, and is here mentioned only because of its exceedingly interesting relationship to nitrogen, phosphorus, and arsenicum. Discovered but not isolated by Sefström, and its compounds investigated by Berzelius, it has only of late years been obtained in the free state and fully studied by Roscoe.

Oxides of Nitrogen.		Oxides of Vanadium.	
N_2O_5, N_2O_4, N_2O_3, N_2O_2, N_2O.		V_2O_5, V_2O_4 V_2O_3, V_2O_2, V_2O.	
Orthophosphates	$R_3'PO_4$	Orthovanadates	$R_3'VO_4$
Pyrophosphates	$R_4'P_2O_7$	Pyrovanadates	$R_4'V_2O_7$
Metaphosphates	$R'PO_3$	Metavanadates	$R'VO_3$

Isomorphous Minerals.

Apatite	$3(Ca_32PO_4),CaFl_2$
Pyromorphite	$3(Pb_32PO_4),PbCl_2$
Mimetesite	$3(Pb_32AsO_4),PbCl_2$
Vanadinite	$3(Pb_32VO_4),PbCl_2$

BORACIC ACID AND OTHER BORATES.

Formula of Boracic Acid H_3BO_3. Molecular weight 62.

The composition of artificial boracic acid is expressed by the formula H_3BO_3 (*Acidum Boricum*, U. S. P.); but at a temperature of 212° F. this body loses the elements of water and yields metaboracic acid, HBO_2, which at higher temperatures becomes boracic anhydride (B_2O_3). The latter acid exists in the jets of steam (*fumerolles* or *suffioni*) that issue from the earth in some districts of Tuscany, and collects in the water of the *lagoni* (lagoons or little lakes) formed at the orifices of the steam-channels. This acid liquid, evaporated by aid of the waste natural steam and neutralized by carbonate of sodium, gives common borax ($2NaBO_2,2HBO_2,9H_2O$), possibly an acid metaborate of sodium with water of crystallization. It occurs "in transparent colorless crystals, sometimes slightly effloresced, with a weak alkaline reaction; insoluble in rectified spirit, soluble in water." Native borax, or *tincal*, and other borates are also found in Thibet, in Nevada, Peru, Chili, and recently in California, in the Clear Lake district. The introduction of the natural borax from California has reduced the price to about one-half its former amount. This borax is represented as forming large portions of the crystalline bed of a dried-up lake. Fused borax readily dissolves metallic oxides, as will have been already noticed in testing for cobalt and manganese. Hence, besides its use in medicine (*Sodii Boras*, U. S. P.), it is employed as a flux in refining and other metallurgic and ceramic operations.

Quantivalence.—The boracic radical is trivalent (BO_3'''), the metaboracic, univalent (BO_2'); they have not been isolated. *The element boron*, like carbon, occurs in the amorphous, graphitoidal, and crystalline conditions. It is a trivalent element (B'''), yielding definite salts, such as the chloride (BCl_3) and fluoride (BF_3). Its atomic weight is 11.

REACTIONS.

First Synthetical Reaction.—To a hot solution of a crystal of borax add a few drops of sulphuric acid and set aside; on cooling, crystalline scales of boracic acid (H_3BO_3) are deposited. They may be purified by collecting on a filter, slightly washing, drying, digesting in hot alcohol, filtering, and setting aside; pure boracic acid (B. P.) is deposited. The acid may also be recrystallized from water. Fifty grains dissolved in one ounce of rectified spirit constitute "Solution of Boracic Acid," B. P.

Boracic acid is a very weak compound. It only slowly decomposes carbonates, and resembles alkaline substances in coloring turmeric brown. Indeed the alkalinity of borax is as great as if it contained no acidulous radical. Boracic acid is said to be itself an antiseptic, but Endemann states that in preserving foods it acts by converting phosphates into acid phosphates, and that the latter are the antiseptic principles.

Second Synthetical Reaction.—Mix together 1 part of boracic acid, 4 of acid tartrate of potassium, and 10 or 20 of water; evaporate to a syrupy consistence, spread on plates, and set aside for dry scales to form. The resulting substance is, in water, far more readily soluble than either of its constituents, and is known as *boro-tartrate of potassium* or *soluble cream of tartar.* The Prussian *tartarus boraxatus* differs from the foregoing French variety in containing 1 part of *borax* to 3 of acid tartrate of potassium.

Analytical Reactions (Tests).

First Analytical Reaction.—Dip a piece of turmeric-paper (paper soaked in tincture of turmeric tubers and dried) into a solution of boracic acid; it is colored brown-red, as by alkalies.

The usual way of applying this test is as follows: Add to a solution of any borate a few drops of hydrochloric acid; immerse half of a slip of turmeric-paper in the liquid, then remove the hydrochloric acid by drying the paper over a flame. Concentrated hydrochloric acid and ferric chloride produce a somewhat similar effect.

Second Analytical Reaction.—To a fragment of a borate or metaborate (borax, for example) in a small dish or watch-glass add a drop of sulphuric acid, and then a little alcohol, warm the mixture and set light to the spirit; the resulting flame will be tinged of a greenish color at its edges by the volatilized boracic acid or boracic anhydride.

The liquid should be well stirred while burning. Salts of copper and some metallic chlorides produce a somewhat similar color. The flame test may also be applied to a little of a mixture of the borax with strong sulphuric acid on a platinum wire. Glycerin may be used in place of sulphuric acid (*Iles*).

Other Analytical Reactions.—In solutions of borax barium salts give a white precipitate of barium metaborate ($Ba2BO_2$) soluble in acids and alkaline salts. Nitrate of silver gives metaborate of silver ($AgBO_2$) soluble in nitric acid and in ammonia. Chloride of calcium, if the solution is not too dilute, gives white borate of calcium.

QUESTIONS AND EXERCISES.

573. Illustrate the relation of vanadium to nitrogen by formulæ of compounds of each element.

574. Describe the preparation of borax.

575. Give the formulæ of boracic acid, metaboracic acid, and borax.

576. Mention the tests for borates or metaborates.

The foregoing acids and other salts contain the only acidulous radicals that are commonly met with in analysis or in ordinary medical or pharmaceutical operations. There are, however, many others which occasionally present themselves. The chief of these will now be shortly noticed; they are arranged in alphabetical order to facilitate reference.

SALTS OF RARER ACIDULOUS RADICALS.

Anemonic Acid.—*Pulsatilla*, U. S. P., is the official name for the herbs of *Anemone Pulsatilla*, *A. pratensis*, and *A. patens*. These. together with several species of *Ranunculus*, on distillation with water yield a heavy, yellow, acrid oil, which, in contact with water, yields crystalline poisonous *anemonin* ($C_{15}H_{12}O_6$) and amorphous *anemonic acid* ($C_{15}H_{14}O_7$).

BENZOIC ACID ($HC_7H_5O_2$) AND OTHER BENZOATES.—Slowly heat a fragment of benzoin (Gum benzoinum) (*Benzoinum*, U. S. P.) in a test-tube; benzoic acid (*Acidum Benzoicum*, U. S. P.) rises in vapor and condenses in small, white, feathery plates and needles, on the cool sides of the tube. If the benzoin is first mixed with twice its weight of sand or roughly powdered pumice-stone, and the heat very cautiously applied, the product will be less likely to be burnt, and a larger quantity be yielded. By repeated sublimation 10 to 15 per cent. may be obtained.

A more economical process is to boil the benzoin with one-fourth of its weight of lime, filter, concentrate, decompose the solution of benzoate of calcium by hydrochloric acid, collect the precipitated benzoic acid, press between paper, dry and sublime in a tube or other vessel.

$$\underset{\substack{\text{Benzoic acid}\\\text{(impure).}}}{2HC_7H_5O_2} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Benzoate of}\\\text{calcium.}}}{Ca2C_7H_5O_2} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\substack{\text{Benzoate of}\\\text{calcium.}}}{Ca2C_7H_5O_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Chloride of}\\\text{calcium.}}}{CaCl_2} + \underset{\substack{\text{Benzoic acid}\\\text{(pure).}}}{2HC_7H_5O_2}$$

There is always associated with the product a minute quantity of a volatile oil (styrol?) of agreeable odor, suggesting that of hay.

Benzoic acid is also prepared on a large scale artificially from naphthalene, one of the crystalline by-products in the distillation of coal for gas. The naphthalene is oxidized by nitric acid to naphthalic or phthalic acid:—

$$\underset{\text{Naphthalene.}}{C_{10}H_8} + \underset{\text{Oxygen.}}{4O_2} = \underset{\text{Phthalic acid.}}{H_2C_8H_4O_4} + \underset{\text{Oxalic acid.}}{H_2C_2O_4}$$

The phthalic acid is neutralized by lime, and the phthalate of calcium heated with hydrate of calcium in a covered vessel at a temperature of about 640° F. for several hours. Benzoate and carbonate of calcium are formed, and from the powder the benzoic acid is set free by action of hydrochloric acid.

$$\underset{\substack{\text{Phthalate of}\\\text{calcium.}}}{2CaC_8H_4O_4} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Benzoate of}\\\text{calcium.}}}{Ca2C_7H_5O_2} + \underset{\substack{\text{Carbonate of}\\\text{calcium.}}}{2CaCO_3}$$

The crystalline deposit formed when essential oil of almonds (hydride of benzoyl or benzoic aldehyd) is exposed to the air is benzoic acid.

$$\underset{\substack{\text{Hydride of}\\\text{benzoyl.}}}{2C_7H_5OH} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Hydrate of}\\\text{benzoyl.}}}{2C_7H_5OHO} \underset{\text{or}}{\text{ or }} \underset{\substack{\text{Benzoic}\\\text{acid.}}}{2HC_7H_5O_2}$$

Benzoic acid is also obtained from hippuric acid (p. 336). Such acid, if not thoroughly purified, may have an urinoid odor. Jacobsen prepares benzoic acid from benzotrichloride (trichloromethylbenzol, $C_6H_5CCl_3$), one of the trichlortoluenes, by heating with glacial acetic acid and chloride of zinc. This acid, if not very highly purified, may give a green color to flame when placed on platinum wire with a little oxide of copper. In artificial benzoic acid the fragrant volatile oil characteristic of the natural acid is, of course, absent; while in some specimens the odor of oil of bitter almond may be detected.

Benzoate of Ammonium.—To a little benzoic acid add a few drops of solution of ammonia; it readily dissolves, forming benzoate of ammonium (*Ammonii Benzoas*, U. S. P.) ($NH_4C_7H_5O_2$).

$$\underset{\text{Benzoic acid.}}{HC_7H_5O_2} + \underset{\text{Ammonia.}}{NH_4HO} = \underset{\text{Benzoate of ammonium.}}{NH_4C_7H_5O_2} + \underset{\text{Water.}}{H_2O}$$

On evaporation, acid crystals or, ammonia being added, neutral crystals of benzoate of ammonium are deposited. Benzoate of sodium (*Sodii Benzoas*, U. S. P.), $NaC_7H_5O_2,H_2O$, may be similarly prepared.

Properties.—Benzoic acid is also soluble in other alkaline liquids, forming benzoates. It is slightly soluble in cold water, more so in hot, and readily soluble in rectified spirits. It melts at 248° F., and boils at 462°, volatilizing with only a slight residue. Heated with lime it yields benzol. It dissolves in cold oil of vitriol without decomposition, is again deposited on dilution, and the traces of odoriferous and other substances present in the acid from benzoin only slightly color the fluid, even on gently warming.

Tests for Benzoates.—To a portion of the above solution of benzoate of ammonium add a drop or two of sulphuric or hydrochloric acid; a white crystalline precipitate of benzoic acid separates. To another portion, carefully made neutral, add a drop or two of neutral solution of perchloride or persulphate of iron; reddish ferric benzoate is precipitated.

Cinnamic Acid ($C_9H_9O_2$).—Benzoic acid is distinguished from an allied body, cinnamic acid (occurring in Balsams of Peru, Tolu, and Storax, and sometimes in Benzoin), by not yielding hydrate of benzoyl (C_7H_5OH) (oil of bitter almonds) when distilled with chromic acid—that is, with a mixture of red chromate of potassium and sulphuric acid—or when rubbed with half its weight of permanganate of potassium. Old hard balsam of tolu yields it on boiling with lime and water and percipitating by hydrochloric acid. Jacobsen makes it artificially by the prolonged reaction of glacial acetic acid and benzodichloride in the presence of chloride of zinc.

CARMINIC ACID ($C_{14}H_{14}O_8$).—This is the coloring principle of cochineal (*Coccus*, U. S. P.). The *carmine* of trade, when unadulterated (*vide* Pharmaceutical Journal, 1859–60, p. 546), is carminic acid united with one or two per cent. of alumina, or, occasionally, of oxide of tin or albumen. It should be wholly soluble in solution of ammonia, giving an apparently clear rich purple fluid. Carmine, with French chalk, or starch, constitutes *face-rouge* or *animal rouge.*

Merrick tests the relative value of several samples of cochineal or carmine by observing how much solution of permanganate of potassium is required to change the color of a decoction to faint pink.

CETRARIC ACID ($H_2C_{34}H_{30}O_{16}$) is the bitter principle of Iceland moss (*Cetraria*, U. S. P.). In the lichen it is associated with much starch.

Chrysophanic Acid ($C_{14}H_{10}O_4$).—This acid is the chief coloring-matter of various species of rhubarb-root (*Rheum*, U. S. P.), and, under the name of *parietinic acid*, of various common yellow lichens. The author also found it to form four-fifths of old "Chrysarobine," a name given by Kemp to the pith, etc. of a leguminous tree (*Andira Araroba*). Chrysarobine or *crysarobin* (*Chrysarobinum*, U. S. P.) is also known as Araroba Powder, Bahia Powder, Brazil Powder, Goa Powder, and Ringworm Powder. Recent chrysarobin has been shown by Liebermann and Seidler to have the formula $C_{30}H_{26}O_7$; this, by oxidation and elimination of water, yields the chrysophanic acid occurring in old chrysarobin. Chrysophanic acid may be obtained in crystals of a golden-yellow color, hence the name (from *χρυσὸς*, *chrusos*, gold, and *φαίνω*, *phainō*, I shine). Its synonyms are *Rhaponticin*, *Rheic acid*, *Rhein*, *Rheumin*, *Rheubarbaric acid*, *Rheubarbarin*, *Rumicin*. Chrysophanic acid, black, red-brown, and red resins (*Aporetine*, *Phæoretine*, and *Erythroretine*), a bitter principle, and tannic acid, are considered to be the conjoint source of the therapeutic properties of rhubarb. Chrysophanic acid is also contained in several species of *Rumex* or *Dock*. "Rumicin" is a name given to a preparation of the root of *Rumex crispus*, or Yellow Dock (*Rumex*, U. S. P.).

Cornic Acid, or Cornin.—This is, according to Geiger, the crystalline bitter principle of the bark (*Cornus*, U. S. P.) of *Cornus florida*. A crystalline resin is also present.

Cyanic Acid (HCyO) and other Cyanates.—The valuable reducing power of cyanide of potassium (KCy) (or ferrocyanide, K_4Fcy) on metallic compounds is due to the avidity with which cyanate (KCyO) is formed.

Process.—Fuse a few grains of cyanide of potassium in a small porcelain crucible, and add powdered oxide of lead; a globule of metallic lead is at once set free, excess of the oxide converting the whole of the cyanide of potassium into cyanate of potassium.

Urea.—Cyanate of potassium (KCNO), or, better, cyanate of lead (Pb2CNO), treated with sulphate of ammonium, yields cyanate of ammonium (NH_4CNO); and solution of cyanate of ammonium, when simply heated, changes to artificial *urea* (CH_4N_2O), the most important constituent of urine, and the chief form in which the nitrogen of food is eliminated from the animal system. The process will be more fully described subsequently in connection with Urea.

Formic Acid ($HCHO_2$).—The red ant (*Formica rufa*) and several other insects, when irritated, eject a strongly acid, acrid liquid, having a composition expressed by the above formula, and which has appropriately received the name of formic acid; it is also contained in the leaves of the stinging-nettle. (According to Church the sting of the wasp is alkaline.)

Process.—It may be artificially prepared by heating equal weights of oxalic acid and glycerin to a temperature of from 212° to 220° F. for fifteen hours, and then distilling the mixture with a considerable volume of water. The formic acid slowly passes over, the glycerin being regenerated. The dilute acid may be concentrated by neutralizing with carbonate of lead, filtering, evaporating to a small bulk, collecting the deposited crystalline formate of lead, drying, decomposing in a current of sulphuretted hydrogen, separating the resulting syrupy acid, and passing air through the product until all sulphuretted hydrogen is removed. The following are the chief reactions:—

$$\underset{\text{Glycerin.}}{C_3H_53HO} + \underset{\substack{\text{Oxalic}\\\text{acid.}}}{H_2C_2O_4} = \underset{\substack{\text{Hydrato-oxalate}\\\text{of glyceryl.}}}{C_3H_5HOC_2O_4} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\substack{\text{Hydrato-oxalate}\\\text{of glyceryl.}}}{C_3H_5HOC_2O_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Glycerin.}}{C_3H_53HO} + \underset{\substack{\text{Formic}\\\text{acid.}}}{HCHO_2} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2}$$

Formic acid may be instructively though not economically prepared by the oxidation of methylic alcohol (wood spirit), just as acetic acid and valerianic acid are obtained from ethylic alcohol and amylic alcohol respectively.

$$\underset{\substack{\text{Wood-}\\\text{spirit.}}}{CH_3HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Formic}\\\text{acid.}}}{HCHO_2} + \underset{\text{Water.}}{H_2O}$$

Tests.—Formic acid does not char when heated alone or with sulphuric acid, but splits up into carbonic oxide gas and water. It is recognized by this property and by its reducing action on salts of gold, platinum, mercury, and silver. It is solid below 32° F.

GALLIC ACID.—See *Tannic Acid.*

HEMIDESMIC ACID.—The supposed active principle of hemidesmus root (*Hemidesmi radix*, B. P.).

HIPPURIC ACID ($HC_9H_8NO_3$) is a constituent of human urine (much increased on taking benzoic acid), but is best prepared from the urine of the horse (hence the name, from ἵππος, *hippos*, a horse), or, better, from that of the cow. To such urine add a little milk of lime, boil for a few minutes, remove precipitated phosphates by filtration, drop in hydrochloric acid until the liquid, after well stirring, is exactly neutral to test-paper, concentrate to about one-eighth the original bulk, and add excess of strong hydrochloric acid; impure hippuric acid is deposited. From a solution of the impure acid in hot water chlorine gas removes the color, and the liquid deposits crystals of pure hippuric acid on cooling. Its constitution is that of *benzoic glycocine*, $C_2H_2H_2(C_7H_5O)NO_2$.

Tests.—To a solution of hippurate add neutral solution of ferric chloride; a brown precipitate (ferric hippurate) results. Salts of silver and mercury give white precipitates. Heat hippuric acid in a test-tube; it chars, benzoic acid sublimes, and vapors of characteristic odor are evolved; they contain, amongst other bodies, hydrocyanic acid and a substance smelling somewhat like Tonka bean. ——The crystalline form of hippuric acid is characteristic; it will be described in connection with the subject of urine.

QUESTIONS AND EXERCISES.

577. Give the preparation, composition, properties, and tests of benzoic acid, employing equations or diagrams.
578. What is the nature of carmine?
579. Name the bitter principle of Iceland moss.
580. Mention the coloring principle of rhubarb.
581. To what is rhubarb considered to owe its medicinal activity?
582. How is cyanate of potassium prepared, how converted into an ammonium salt, and what are the relations of the latter to urea?
583. Give the formulæ of cyanic acid, cyanate of ammonium, and urea.
584. What is the chemical formula of formic acid?
585. Describe the artificial production of formic acid.
586. Describe the relation of formic acid to wood spirit.
587. State the sources, characters, and tests of hippuric acid.

Hydroferrocyanic Acid ($H_4Fe''Cy_6$, or H_4Fcy'''') and other Ferrocyanides.—The ferrocyanide of most interest is that of potassium (*Potassii Ferrocyanidum*, U. S. P.), the yellow prussiate of potash (*Potassæ Prussias Flava*, B. P.) ($K_4FeC_6N_6,3H_2O$), the formation of which was alluded to in connection with hydrocyanic acid (see page 276). It cannot be regarded as simply a double salt of cyanide of potassium with cyanide of iron ($FeCy_2,4KCy$), its chemical properties being entirely different from either of those substances; moreover, unlike cyanide of potassium, it is not poisonous. Most of its reactions point to the conclusion that its iron and cyanogen are intimately united to form a definite quadrivalent radical appropriately termed *ferrocyanogen* ($FeCy_6$, or Fcy). One part of ferrocyanide of potassium in 20 of water forms the official "Solution of Yellow Prussiate of Potash," B. P.

Tests.—Many of the ferrocyanides are insoluble, and are therefore precipitated when solution of ferrocyanide of potassium is added to the various salts. Those of iron and copper, being of characteristic color, are adopted as tests of the presence of the metals or of the ferrocyanogen, as the case may be.

To solution of ferrocyanide of potassium add a ferric salt; ferrocyanide of iron (Fe_4Fcy_3) (Prussian blue) is precipitated.

$$3K_4Fcy + 2(Fe_23SO_4) = Fe_4Fcy_3 + 6K_2SO_4.$$

To another portion add solution of a copper salt; reddish-brown ferrocyanide of copper (Cu_2Fcy) is precipitated.

Note.—The ferrocyanogen in ferrocyanide of potassium is broken up when the salt is heated with sulphuric acid, *carbonic oxide* being evolved if the acid is strong (that is, ordinary oil of vitriol —H_2SO_4 with 3 to 4 per. cent of water), and *hydrocyanic acid* if weak:—

$$K_4FeC_6N_6,3H_2O + 3H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

$$2K_4FeCy_6 + 6H_2SO_4 + xH_2O = FeK_2FeCy_6 + 6KHSO_4 + 6HCy + xH_2O.$$

Hydrocyanic Acid has already been described. (*Vide* p. 277.)

Carbonic Oxide (CO).—Heat two or three fragments of ferrocyanide of potassium with eight or ten times their weight of sulphuric acid, and as soon as the gas begins to be evolved remove the test-tube from the flame; for the action, when once set up, proceeds somewhat tumultuously. Ignite the carbonic oxide at the mouth of the tube; it burns with a pale blue flame, the product of combustion being carbonic acid gas (CO_2).

Carbonic oxide is a direct poison. It is generated whenever coke, charcoal, or coal burns with an insufficient supply of air. Hence the danger of open fires in the more or less closed apartments of ordinary dwellings.

Carbonic oxide may also be obtained from oxalic acid. (*Vide* p. 314.)

HYDROFERRIDCYANIC ACID ($H_6Fe'''_2Cy_{12}$, or $H^{\text{I}}_6Fdcy^{\text{VI}}$) AND OTHER FERRIDCYANIDES.—Pass chlorine gas slowly through solution of ferrocyanide of potassium until the liquid, after frequent shaking, ceases to give a blue precipitate, when a minute portion is taken out on the end of a glass rod and brought into contact with a drop of a dilute solution of a ferric salt; it now contains ferridcyanide of potassium ($K_6Fe'''_2Cy_{12}$, or $K^{\text{I}}_6Fdcy^{\text{VI}}$), *red prussiate of potash* (B. P.), as it is termed from the color of its crystals. Excess of chlorine must be carefully avoided, as chloride of cyanogen and other compounds are then formed.

$$2K'_4Fe''Cy'_6 + Cl'_2 = 2K'Cl' + K'_6Fe'''_2Cy'_{12}.$$

Another Process.—To a cold solution of yellow prussiate of potash so much hydrochloric acid is added as will take two atoms of potassium from two molecules of the salt, and then a cold clear solution of bleaching-powder till ferric chloride gives no reaction. Any excess of acid is then neutralized with chalk and the solution evaporated to crystallization (Rhien).

Note.—The removal of two atoms of potassium from the ferrocyanide is the only change of composition that occurs; but the ferrocyanogen is altered in quality, its iron passing from the ferrous to the ferric condition, from bivalent to trivalent activity, altered to a condition in which it no longer precipitates ferric salts, but, on the other hand, gives a dark-blue precipitate with ferrous salts. The radical is distinguished as *ferridcyanogen.*

Ferridcyanide of potassium may also be prepared by a modification of the foregoing method in which nascent instead of free chlorine is employed (Wenzell). Take of Bichromate of Potassium 1 part, Ferrocyanide of Potassium Cryst. 5.72 parts, Hydrochloric Acid, of spec. grav. 1.16, 3 parts by weight, Water 60 parts. Dissolve the two salts in hot water, add the acid, heat to boiling, continuing the ebullition, replacing the water evaporated during the process until a portion of the filtered liquid is not precipitated on the addition of solution of ferric chloride. When reaction is completed, filter the liquid and wash the hydrate of chromium, unite the liquids, and concentrate to crystallization. If the evaporated liquid possess an acid reaction, the addition of caustic potash, in sufficient quantity to cause a weak alkaline reaction, will greatly facilitate the subsequent crystallization.

$$6(K_4FeCy_6) + K_2Cr_2O_7 + 8HCl = 3(K_6Fe_2Cy_{12}) \\ + 8KCl + H_2O + Cr_2 6HO.$$

Test.—To a portion of the solution add solution of ferrous sulphate; a precipitate falls. This precipitate is ferridcyanide of iron (Turnbull's blue), $Fe''_3Fe'''_2Cy'_{12}$, or $Fe^{II}_3Fdcy^{VI}$.

$$K_6Fdcy + 3FeSO_4 = Fe_3Fdcy + 3K_2SO_4.$$

It will be noticed that the change in the condition of the iron keeps up the balance of the atomic values of the various parts of the radicals or of the salts; the quantivalential equilibrium is maintained.

A solution of 1 part of ferridcyanide of potassium in 20 of water constitutes the "Solution of Red Prussiate of Potash," B. P.

HYDROFLUORIC ACID (HF) AND OTHER FLUORIDES.—Molecular weight of HF, 20. The chief use of hydrofluoric acid is in the etching on glass. The operation, performed on the small scale, also constitutes the best test for fluorine, the elementary radical of all fluorides.

Process and Test.—Warm any odd piece of window-glass, having an inch or two of surface, until a piece of beeswax rubbed on one side yields a thin oily film. When cool make a cross, letter, or other mark on the glass by pressing a pointed piece of wood, a penknife, or file, through the wax. Place a few grains of powdered fluor spar, the commonest natural fluoride, in a porcelain crucible (or a lead cup), add a drop or two of sulphuric acid, cover the crucible with the prepared glass, waxed side downwards, and gently warm the bottom of the crucible in a fume-chamber or in the open air, in such a way as not to melt the wax. After a few minutes remove the glass, wash the waxed side by pouring water over it, scrape off most of the wax, then warm the glass, and wipe off the remainder; the marks made through the wax will be found to be permanently etched on the glass; the acid has eaten into or *etched* (from the German *ätzen*, to corrode) the glass.

In the above operation the fluoride of calcium and sulphuric acid yield hydrofluoric acid, thus:—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The hydrofluoric acid gas and the silica of the glass then yield gaseous fluoride of silicon (SiF_4), which escapes, and water, thus:—

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

The silica, being removed from the glass, leaves furrows or etched portions.

Note.—In the experiment just described, the liberated hydrofluoric acid also attacks the siliceous glazing of the porcelain crucible: so that in important cases, where search is made for very small quantities of fluorine, vessels of platinum or lead must be employed.

Uses.—The aqueous solution of hydrofluoric acid used by etchers, and commonly termed simply hydrofluoric acid, or "fluoric" acid, is prepared in leaden stills and receivers, and kept in leaden or gutta-percha bottles. Except these materials, as well as platinum and fluor spar, hydrofluoric acid rapidly attacks any substance of which bottles and basins are usually made. It quickly cauterizes the skin, producing a painful, slow-healing sore.

Quantivalence.—The atom of fluorine, like that of chlorine, bromine, or iodine, is univalent (F'). The great analogy existing between these radicals extends to their compounds.

Fluorine is said to be a colorless gas; but, from the avidity with which it combines with all elements (except oxygen), it is so difficult of isolation as hitherto to preclude satisfactory study of its physical properties.

HYPOPHOSPHOROUS ACID (H_3PO_2, or HPH_2O_2) AND OTHER HYPOPHOSPHITES.—Boil together, in a fume-chamber, a grain or two of phosphorus, a few grains of slaked lime, and about a quarter of an ounce of water until phosphoretted hydrogen, a spontaneously inflammable, badly-smelling gas, ceases to be evolved. The lime must not be in great excess or the hypophosphite will be converted into phosphate as fast as formed.

The mixture, filtered, and excess of lime removed by carbonic acid gas, yields solution of hypophosphite of calcium ($Ca2PH_2O_2$) (*Calcii Hypophosphis*, U. S. P.).

$$2P_4 + 6H_2O + 3CaH_2O_2 = 3(Ca2PH_2O_2) + 2PH_3.$$

The solution, when concentrated by evaporation, has been known to explode, probably from formation of phosphoretted hydrogen. This may be prevented, it is said, by evaporating at a low temperature, especially towards the close of the operation; or by adding alcohol, which decomposes any traces of liquid phosphoretted hydrogen (PH_2) or solid phosphoretted hydrogen (P_2H) which possibly may be present, and to which it is conceivable explosion may be due. The aqueous solution may conveniently contain one-fourth or one-third of real acid.

Phosphoretted Hydrogen (PH_3).—The above reaction is also that by which phosphoretted hydrogen, the third hydride of phosphorus, may be prepared. If the gas is to be collected, the phosphorus and water may first be boiled in a flask until a jet of spontaneously inflammable phosphorus vapor escapes, with steam, from the end of the attached delivery-tube. Strong solution of caustic potash or soda is next very gradually poured into the flask through a funnel tube previously fitted into the cork, the liquid being kept boiling. Phosphoretted hydrogen is then evolved, and, if the delivery-tube dip under water, may be collected, or allowed to slowly pass up through the water bubble by bubble so as to form the peculiar rings of smoke (phosphoric anhydride) characteristic of the experiment.

Hypophosphite of calcium ($Ca2PH_2O_2$) (*Calcii Hypophosphis*, U. S. P.) may be obtained in crystals by evaporating and slowly cooling; but the solution is usually at once evaporated to dryness, a white pulverulent salt being obtained. The Hypophosphite of Potassium (*Potassii Hypophosphis*, U. S. P.) (KPH_2O_2) may be obtained in the same way from its hydrate, and many other hypophosphites ($Mg2PH_2O_2,6H_2O$, $Fe2PH_2O_2,6H_2O$, etc.) similarly from other hydrates, or by double decomposition of the calcium salt and carbonates.

Hypophosphite of sodium ($NaPH_2O_2,H_2O$) (*Sodii Hypophosphis*, U. S. P.) may be made by decomposing solution of hypophosphite of calcium by carbonate of sodium, filtering, and evaporating to dryness. It is a white, granular, deliquescent substance.

$$Ca2PH_2O_2 + Na_2CO_3 = 2NaPH_2O_2 + CaCO_3.$$

When heated, the water is first evolved, then hydrogen and spontaneously inflammable phosphoretted hydrogen, and a mixture of pyrophosphate and metaphosphate of sodium remains (Rammelsberg).

$$5NaPH_2O_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2.$$

Hypophosphorous acid, the hydrogen hypophosphite, may be prepared by decomposing the barium salt with sulphuric acid or the calcium salt by oxalic acid; hypophosphite of quinine by dissolving the alkaloid in hypophosphorous acid, or by decomposing sulphate of quinine by hypophosphite of barium. Hypophosphite of Iron ($Fe_2 6PH_2O_2$) (*Ferri Hypophosphis*, U. S. P.) may be obtained by dissolving ferric hydrate in cold aqueous hypophosphorous acid and evaporating the solution.

The hypophosphites are often used in medicine in the form of syrups (*Syrupus Hypophosphitum*, U. S. P., and *Syr. Hypophosphitum cum Ferro*, U. S. P.). The term hypophosphite is in allusion to the smaller amount (*ὑπὸ*, *hupo*, under or deficiency) of oxygen in these compounds (R'_3PO_2) than in the phosphites (R_3PO_3), a class of salts having again less oxygen in their molecules than exists in those of the phosphates (R_3PO_4). The prefix *hypo* has similar significance in such words as hyposulphite and hypochlorite.

Tests.—To a portion of the above solution of hypophosphite of calcium add solution of chloride of barium, chloride of calcium, or acetate of lead; in neither case is a precipitate obtained, whereas soluble phosphates and phosphites yield white precipitates of phosphate or phosphite of barium, calcium, or lead. To other portions add solutions of nitrate of silver and mercuric chloride; the respective metals are precipitated as by phosphites. To another small portion add zinc and dilute sulphuric acid; hydrogen and phosphoretted hydrogen are evolved as from phosphites. To another portion add sufficient oxalic acid to remove the calcium; filter; to the solution of hypophosphorus acid add solution of sulphate of copper, and slowly warm the mixture; solid brown cuprous hydride (Cu_2H_2) is precipitated: increase the heat to the boiling-point; hydrogen is evolved and metallic copper set free. Heat a small quantity of a solid hypophosphite on the end of a spatula in a flame; it splits up into pyrophosphate, a little metaphosphate, hydrogen, phosphoretted hydrogen, and, sometimes, water, burning with a phosphorescent light—the official hypophosphite of calcium yielding about 80 per cent. of residue.

$$7(Ca2PH_2O_2) = 3Ca_2P_2O_7 + Ca2PO_3 + 6PH_3 + H_2O + 4H_2.$$

To an acid solution of hypophosphite add solution of a permanganate. It is instantly decolorized. The same effect follows its addition to an acid solution of a phosphite, but not to that of an ortho-, meta-, or pyrophosphate.

HYPOSULPHUROUS ACID ($H_2S_2O_3$) AND OTHER HYPOSULPHITES.—The only hyposulphite of much interest in pharmacy is the sodium salt (*Sodii Hyposulphis*, U. S. P.) ($Na_2S_2O_3$,-$5H_2O$). Hyposulphites may be regarded as *thiosulphates* (*e. g.*, H_2SO_3S).

Process.—Heat together gently, or set aside in a warm place, a mixture of solution of sulphite of sodium (Na_2SO_3) and a little powdered sulphur; combination slowly takes place, and hyposulphite of sodium is formed. The solution, filtered from excess of sulphur, readily yields crystals. (The solution of sulphite of sodium may be made by saturating a solution of soda with sulphurous acid gas.)

Use of Hyposulphite of Sodium in Quantitative Analysis.—In the British Pharmacopœia hyposulphite of sodium is given as a reagent for the quantitative estimation of free iodine in volumetric analysis. To a few drops of iodine-water add cold mucilage of starch; a deep-blue color (starch iodide) is produced. To the product add solution of hyposulphite of sodium until the blue color just disappears. This absorption of iodine is sufficiently definite and delicate to admit of application for quantitative purposes. It depends on the combination of the iodine with half of the sodium in two molecules of the hyposulphite, the hyposulphurous radicals of the two molecules apparently coalescing to form a new radical, the tetrathionic (from τέτρας, *tetras*, four, and θεῖον, *theion*, sulphur), tetrathionate of sodium ($Na_2S_4O_6$) and iodide of sodium being formed.

Sulphur Oxyacids.—It will be as well here to give the formulæ of other oxyacids of sulphur, forming with the four already mentioned a series that is as useful as the series of compounds of nitrogen and oxygen in illustrating the soundness of Dalton's atomic theory (p. 50).

Hydrosulphurous Acid	H_2SO_2
Sulphurous Acid	H_2SO_3
Sulphuric Acid	H_2SO_4
Hyposulphurous Acid	$H_2S_2O_3$
Dithionic Acid	$H_2S_2O_6$
Trithionic Acid	$H_2S_3O_6$
Tetrathionic Acid	$H_2S_4O_6$
Pentathionic Acid	$H_2S_5O_6$

Use of "Hypo" in Photography.—The sodium hyposulphite is largely used in photography to dissolve chloride, bromide, or iodide of silver off plates which have been exposed in the camera. Prepare a little chloride of silver by adding a chloride (chloride of sodium) to a few drops of solution of nitrate of silver. Collect the precipitated chloride on a filter, wash, and add a few drops of solution of hyposulphite of sodium; the silver salt is dissolved, solution of double hyposulphite of sodium and silver being formed. The solution of this double hyposulphite has a remarkably sweet taste, sweeter than syrup, if the solution is strong. The double hyposulphite of sodium and gold is employed for giving a pleasant tint to photographic prints.

Test.—To solution of a hyposulphite add a few drops of dilute sulphuric or other acid; hyposulphurous acid is set free, but at once begins to decompose into sulphurous acid, recognized by its odor, and free sulphur ($2H_2S_2O_3 = 2H_2SO_3 + S_2$). This reaction constitutes the best test for hyposulphites. Another good test of a soluble simple hyposulphite is its power of dissolving chloride of silver with production of a more or less sweet solution.

QUESTIONS AND EXERCISES.

588. Give the formula of ferrocyanide of potassium.

589. What is the supposed constitution of ferrocyanide of potassium?

590. Enumerate the tests for ferrocyanogen.

591. What are the respective reactions of ferrocyanide of potassium with strong and weak sulphuric acid?

592. Mention and explain a common source of carbonic oxide in households. What is the product of its combustion?

593. Write equations or diagrams illustrative of the changes effected on ferrocyanide of potassium during its conversion into ferridcyanide.

594. By what reactions may the presence of a ferridcyanide in a solution be demonstrated?

595. State the difference between Prussian blue and Turnbull's blue.

596. Describe the source, mode of preparation, chief use of, and test for hydrofluoric acid.

597. Illustrate by a diagram the preparation and composition of hyposulphite of sodium.

598. Mention the uses and characteristic reactions of hyposulphite of sodium.

599. Give the names and formulæ of eight acids, each containing hydrogen, sulphur and oxygen.

LACTIC ACID ($HC_3H_5O_3$) AND OTHER LACTATES.—Lactic acid occurs naturally in willow-bark (Dott). When milk turns sour its sugar has become converted into an acid appropriately termed lactic (*lac, lactis*). Other saccharine and amylaceous substances also by fermentation yield lactic acid. The hydrogen lactate (lactic acid) is official (*Acidum Lacticum*, U. S. P.).

Process.—Lactate of calcium and lactic acid may be prepared as follows: Mix together eight parts of sugar, one of common cheese, three of chalk, and fifty of water, and set aside in a warm place (about 80° F.) for two or three weeks;

a mass of small crystals of lactate of calcium results. Remove these, recrystallize from hot water, decompose by sulphuric acid, avoiding excess, digest in alcohol, filter off the sulphate of calcium, evaporate the clear solution to a syrup; this residue is lactic acid; when of sp. gr. 1.212 it contains 75 per cent. of real acid.

Lactate of Iron (*Ferri Lactas*, U. S. P.; $Fe2C_3H_5O_3,3H_2O$) may be made by digesting iron filings in warm diluted lactic acid (1 acid to 16 water) till effervescence of hydrogen ceases, filtering and setting aside to cool and crystallize. The crystals are collected, washed with alcohol, and dried. This ferrous lactate occurs in greenish-white crystalline crusts or grains, of a mild, sweetish, ferruginous taste, soluble in forty-eight parts of cold and twelve of boiling water, but insoluble in alcohol. Exposed to heat, it froths up, gives out thick, white, acid fumes, and becomes black, sesquioxide of iron being left. If it be boiled for fifteen minutes with nitric acid of the specific gravity 1.20, a white, granular deposit of mucic acid will occur on the cooling of the liquid.

Tests.—No single reaction of lactic acid is sufficiently distinctive to form a test. The crystalline form of the lactate of calcium, as seen by the microscope, is characteristic. The production of this salt, and the isolation of the syrupy acid itself, are the only means, short of quantitative analysis, on which reliance can be placed. It is soluble in water, alcohol, and ether, but almost insoluble in chloroform. It is only slightly colored by cold sulphuric acid.

A variety of lactic acid has been obtained from the juice of fish; it is termed *sarcolactic* acid (from *σάρξ*, *σαρκὸς*, *sarx*, *sarcos*, flesh). Unlike lactic acid, it is precipitated by solution of sulphate of copper.

MALIC ACID ($H_3C_4H_3O_5$) AND OTHER MALATES (from *malum*, an apple).—The juice of unripe apples, gooseberries, currants, rhubarb stalks, strawberries, grapes, etc. contains malic acid and malate of potassium. When isolated it occurs in deliquescent prismatic crystals.

Tests.—Malate of calcium ($CaHC_4H_3O_5$) is soluble in water; hence the aqueous solution of malic acid or other malate is not precipitated by lime-water or chloride of calcium; but on adding spirit of wine a white precipitate falls, owing to the insolubility of the calcium malate in alcohol. Malates are precipitated by lead-salts; on warming the malate of lead with acetic acid it dissolves, separating out in acicular crystals on cooling. If the mixture be heated without acid, the malate of lead agglutinates and fuses.

Hot strong sulphuric acid chars malic acid far less readily than it does nearly all other organic acids.

Asparagin ($C_4H_8N_2O_3,H_2O$).—This proximate principle of plants occurs in many vegetable juices, and doubtless plays a very important part in their nutrition. It is deposited in crystals when the fresh juices of asparagus, marshmallow, etc. are rapidly evaporated. It is noticed here because malic acid is readily obtained from it by oxidation, nitrogen being eliminated, and because its exact natural position among chemical substances is not yet well made out. The atoms of its molecule are those of aspartate of ammonium ($NH_4C_4H_6NO_4$), into which it is converted when its solution is long boiled. Decomposed by aid of ferments, asparagin, absorbing hydrogen, yields succinate of ammonium $(NH_4)_2C_4H_4O_4$. Such reactions as these and the formation of lactic acid from sugars should suggest to the student possible modes in which chemical changes take place in the plant-department of the vast laboratory of nature.

MECONIC ACID ($H_3C_7HO_7$).—Opium contains meconic acid (from μήκων, *mekōn*, a poppy) partially combined with morphine. To concentrated infusion of opium nearly neutralized by ammonia add solution of chloride of calcium; meconate of calcium is precipitated. Wash the precipitate, place it in a small quantity of hot water, and add a little hydrochloric acid; the clear liquid (filtered, if necessary) deposits scales of meconic acid on cooling.

Tests.—To solution of meconic acid or other meconate, or to infusion of opium, add a neutral solution of ferric chloride; a red solution of meconate of iron is produced. To a portion of the mixture add solution of corrosive sublimate; the color is not destroyed; to another portion add hydrochloric acid; the color is discharged. (These reagents act on sulphocyanate of iron, which is of similar tint, in exactly the opposite manner.) To another portion add a drop of a dilute acid and boil; the color is not discharged. (A solution of ferric acetate, which is of similar color, *is* decomposed on boiling, giving a colorless fluid and a red precipitate of ferric oxyacetate.)

The normal meconates of potassium, sodium, and ammonium are soluble in water, the acid meconates very slightly soluble, the meconates of barium, calcium, lead, copper, and silver insoluble in water, but soluble in acetic acid.

METAPHOSPHORIC ACID (HPO_3) AND OTHER METAPHOSPHATES.—Prepare phosphoric anhydride (P_2O_5) by burning a small piece of phosphorus in a porcelain crucible placed on a plate and covered by an inverted test-glass tumbler, half-pint measure-glass, or some such vessel. After waiting a few minutes for the phosphoric anhydride to fall, pour a little water on the plate and filter the liquid; the product is solution of metaphosphoric acid (from μετὰ, *meta*, a preposition denoting change).

$$P_2O_5 + H_2O = 2HPO_3.$$

Tests.—To solution of metaphosphoric acid add ammonio-nitrate of silver, or to a neutral metaphosphate add solution of nitrate of silver; a white precipitate ($AgPO_3$) is obtained. This reaction sufficiently distinguishes metaphosphates from the ordinary phosphates or orthophosphates (from ὀρθὸς, *orthos*, straight), as the common phosphates may, for distinction, be termed (which give, it will be remembered, a *yellow* precipitate with nitrate of silver). Another variety of phosphates shortly to be considered, the pyrophosphates, also gives a white precipitate with nitrate of silver. To the solution of metaphosphoric acid obtained as above, or by the action of acetic acid on a metaphosphate, add an aqueous solution of white of egg; coagulation of the albumen ensues. Neither orthophosphoric nor pyrophosphoric acid coagulates albumen. When mixed with an equal volume of Tincture of Chloride of Iron, meta- and pyrophosphoric acids give a precipitate after some time (U. S. P.). Boil the aqueous solution of metaphosphoric acid for some time; on testing the solution the acid will be found to have been converted into orthophosphoric acid:—

$$HPO_3 + H_2O = H_3PO_4 \text{ (orthophosphoric acid).}$$

The ordinary medicinal phosphoric acid is made from phosphorus and nitric acid, the liquid being evaporated to a syrupy consistence to remove the last traces of nitric acid. It may contain pyrophosphoric and metaphosphoric acids, if the heat employed be high enough to remove the elements of water:—

$$2H_3PO_4 - H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid).}$$
$$H_3PO_4 - H_2O = HPO_3 \text{ (metaphosphoric acid).}$$

On redilution the metaphosphoric acid only slowly reabsorbs water. If, therefore, on testing, metaphosphoric be found to be present, the solution should be boiled until conversion to orthophosphoric acid has occurred.

NITROUS ACID (HNO_2) AND OTHER NITRITES.—Strongly heat a fragment of nitrate of potassium or of sodium on a piece of platinum foil; oxygen is evolved and nitrite of potassium remains.

Test.—Dissolve the residue in water, add a few drops of dilute sulphuric acid, then a little weak solution of iodide of potassium, and, lastly, some mucilage of starch; the deep-blue compound of iodine and starch is at once produced. Repeat this experiment, using nitrate of potassium instead of nitrite; no blue color is produced.

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2.$$

Tests for Nitrites in Water.—This liberation of iodine by nitrites and not by nitrates is a reaction of considerable value in searching for nitrites in ordinary drinking-waters, the occurrence of such salts being held to indicate the presence of nitrogenous organic matter in a state of oxidation or decay. The sulphuric acid used in the operation must be pure, and the iodide of potassium free from iodate. If much organic matter is present, however, the nitric acid liberated by the sulphuric may be reduced to nitrous acid. It is perhaps best, therefore, to add acetic acid, and (Fresenius) distil over 10 or 20 per cent. of the water and apply the test to this distillate. Very dilute solutions of nitrous acid may thus be distilled without the slightest decomposition.

Commercial Nitrous Acid.—The liquid commonly termed in pharmacy "nitrous acid" is simply nitric acid impure from the presence of nitrous acid.

The only nitrite used in medicine is a nitrite of an organic basylous radical, ethyl; nitrite of ethyl ($C_2H_5NO_2$), or nitrous ether, is one of the chief constituents of "*sweet spirit of nitre*" (*Spiritus Ætheris Nitrosi*, U. S. P.; *vide* Index).

OPHELIC ACID ($C_{13}H_{20}O_{10}$).—This is one of the principles to which the herb *Ophelia chirata*, or Chiretta (*Chirata*, U. S. P.), owes its bitterness. It is an amorphous yellow body. Another is *Chiratin* ($C_{26}H_{48}O_{15}$), decomposable by hydrochloric acid into *Chiratogenin* ($C_{13}H_{24}O_3$) and ophelic acid (Höhn).

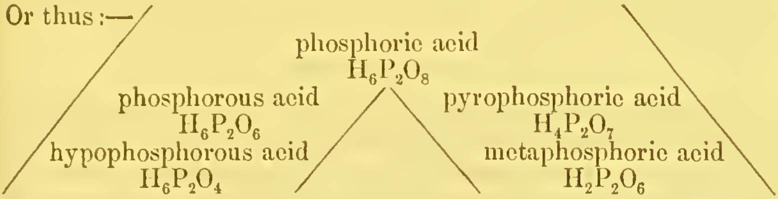
PHOSPHOROUS ACID (H_3PO_3, or H_2PHO_3).—It is necessary to notice this compound in order that the reader may have brought before him the three acids of phosphorus, namely, phosphoric acid (H_3PO_4), phosphorous acid (H_2PHO_3), and hypophosphorous acid (HPH_2O_2): it will be noticed that in composition they differ from each other simply in the proportion of oxygen, the molecules containing four, three, and two atoms respectively. In constitution they differ by the hypothetical phosphoric radical or grouping being trivalent, the phosphorous bivalent, and the hypophosphorous radical univalent. These three acids and corresponding salts must not be confounded with pyrophosphoric and metaphosphoric acids and salts; the former are acids of phosphorus; the latter, varieties of phosphoric acid; the former, in composition, differ from each other in the proportion of oxygen they contain; the latter, by the elements of water:—

Acids of Phosphorus.		*Varieties of Phosphoric Acid.*	
H_3PO_4	phosphoric acid.	H_3PO_4	(ortho)phosphoric acid.
H_2PHO_3	phosphorous acid.	$H_4P_2O_7$	pyrophosphoric acid.
HPH_2O_2	hyphosphorous acid.	HPO_3	metaphosphoric acid.

When hypophosphorous acid is exposed to the air, oxygen is absorbed and phosphorous acid results; by prolonged exposure more oxygen is absorbed and phosphoric acid is obtained. When phosphoric acid, or rather, for distinction, orthophosphoric acid, is heated, every two molecules yield the elements and a molecule of water, and pyrophosphoric acid results; by prolonged exposure to heat more water is evolved, and metaphosphoric acid is obtained. These differences will be further evident if the formulæ be written empirically, nearly all being doubled, thus:—

$H_6P_2O_4$	hypophosphorous acid.
$H_6P_2O_6$	phosphorous acid.
$H_6P_2O_8$	phosphoric acid, or orthophosphoric acid.
$H_4P_2O_7$	pyrophosphoric acid.
$H_2P_2O_6$	metaphosphoric acid.

Or thus:—



From the central compound, phosphoric acid, the acids of phosphorus differ by regularly diminishing proportions of the element oxygen (see previous page), the varieties of phosphoric acid by regularly diminishing proportions of the elements of water.

Prepare phosphorus acid by exposing a moist stick of phosphorus to the air; a thin stream of heavy white vapor falls, which contains the acid in question. The best method of collection is to place the stick in an old test-tube having a hole in the bottom, to support this tube by a funnel or otherwise, the neck of the funnel being supported in a bottle, test-glass, or tube, at the bottom of which is a little water. Having collected some phosphorous acid in this way, apply the various tests already alluded to under *Hypophosphorous Acid*, first carefully neutralizing the phosphorous acid by an alkali. The means by which the varieties of phosphoric acid are distinguished have been given under *Metaphosphoric Acid.* Associated with the phosphorous acid, prepared as above stated, there is said to be an acid having the formula H_2PO_3, and termed *hypophosphoric acid.* Its anhydride would be P_2O_4.

Other soluble phosphites are prepared by neutralizing phosphorous acid with alkalies, and the insoluble phosphites by double decomposition.

PYROGALLIC ACID.—See *Tannic Acid.*

PYROPHOSPHORIC ACID ($H_4P_2O_7$) AND OTHER PYROPHOSPHATES.—Heat ordinary phosphate of sodium (Na_2HPO_4,-$12H_2O$) in a crucible; water of crystallization is first evolved, and dry phosphate (Na_2HPO_4) remains. Continue the heat to redness; two molecules of the salt yield one molecule of water, and a salt having new properties is obtained:—

$$2Na_2HPO_4 - H_2O = Na_4P_2O_7.$$

It is termed pyrophosphate of sodium, in allusion to its origin (πῦρ, *pūr*, fire). From its solution in water it may be obtained in prismatic crystals ($Na_4P_2O_7,10H_2O$), *Sodii Pyrophosphas*, U. S. P. Phosphoric acid itself is similarly affected by heat, $2H_3PO_4 - H_2O = H_4P_2O_7$ (pyrophosphoric acid), though metaphosphoric acid is also formed. Other pyrophosphates are produced in a similar way, or by double decomposition and precipitation, or by neutralizing pyrophosphoric acid by an oxide, hydrate, or carbonate. Possibly the pyrophosphates are only compounds of orthophosphates with metaphosphates:—

$$Na_4P_2O_7 = Na_3PO_4,NaPO_3.$$

Tests.—To solution of a pyrophosphate add solution of nitrate of silver; white pyrophosphate of silver ($Ag_4P_2O_7$) falls as a dense white powder, differing much in appearance from the white gelatinous metaphosphate of silver or the yellow orthophosphate. To pyrophosphoric acid, or to a pyrophosphate mixed with acetic acid, add an aqueous solution of albumen (white of egg); no precipitate occurs. Metaphosphoric acid, it will be remembered, gives a white precipitate with albumen.

QUESTIONS AND EXERCISES.

600. What are the sources of lactic acid?

601. How is lactic acid usually prepared?

602. Name some of the plants in which malic acid is found.

603. Whence is meconic acid derived?

604. By what process may meconic acid be isolated?

605. Which is the best test for the meconic radical?

606. Distinguish meconates from sulphocyanates.

607. Give the mode of manufacture of hyphophosphites.

608. How is phosphoretted hydrogen prepared?

609. By what ready method may metaphosphoric acid be obtained for experimental purposes?

610. Name the tests for metaphosphates.

611. How may meta- or pyrophosphoric acid be converted into orthophosphoric acid?

612. Describe the preparation of phosphorous acid.

613. State the relations which the acids of phosphorus bear to each other.

614. How are pyrophosphates prepared?

615. Offer two views of the constitution of pyrophosphates.

616. Define, by formulæ, metaphosphates, pyrophosphates, orthophosphates, phosphites, and hypophosphites.

617. Mention the tests by which meta-, pyro-, and orthophosphates are analytically distinguished.

618. Name the reactions by which hypophosphites and phosphites are detected.

Silicic Acid (H_4SiO_4) and other Silicates.—Silicates of various kinds are among the commonest of minerals. The various *clays* are aluminium silicates; the volcanic substance termed *pumice-stone* is a porous silicate of aluminium and of alkali-metals or alkaline-earth metals; *meerschaum* is an acid silicate of magnesium; the ordinary *sandstones* are chiefly silica; *sand*, *flint*, *quartz*, *agate*, *chalcedony*, and *opal* are silicic anhydride or *silica* (SiO_2). *Tripoli*, a polishing powder now found in many other countries than Tripoli, consists of infusorial skeletons of nearly pure silica. *Bath brick*, used in knife-polishing, is a silico-calcareous deposit found in the estuary at Bridgewater and other places. *Asbestos* or *amianth* is a fibrous silicate of calcium and magnesium, the length of the fibres being from less than one inch to five feet. A single silk-like fibre can easily be fused, but, even in very small masses, and for all practical purposes, asbestos is infusible and, of course, incombustible. It is also a bad conductor of heat. It is already largely used in piston-rods and joints and for steam apparatus generally; as a covering for boilers to prevent loss of heat by radiation; and for so lining ceilings, floors, and other partitions as to render rooms, etc. fire-proof. Artificial silicates are familiar under the forms of *glass* and *earthenware*. Common English window-glass is usually silicate of calcium, sodium, and aluminium; French glass, silicate of calcium and sodium; Bohemian, chiefly silicate of potassium and calcium; English flint- or crystal-glass for ornamental, table, and optical purposes is mainly silicate of potassium and lead. Earthenware is mostly silicate of aluminum (clay), with more or less of silicate of calcium, sodium, and potassium, and, in the commoner forms, silicates of iron. The various kinds of *porcelain* (China, Sèvres, Meissen, Berlin, English), *Wedgwood-ware*, and *stoneware* are varieties of earthenware. *Kaolin* or *China Clay*, which is disintegrated *felspar*, not more common in China than in Devonshire and Cornwall, is the clay which yields the finest translucent porcelain. *Crucibles*, *bricks*, and *tiles* are clay silicates. *Mortar* is essentially silicate of calcium. *Portland*, *Roman*, and other hydraulic *cements* are silicates of calcium with more or less silicate of aluminium.

Mix together a few grains of powdered flint or sand with about five or six times its weight of carbonate of sodium and an equal quantity of carbonate of potassium, and fuse a little of the mixture on platinum-foil in the blowpipe-flame; the product is a kind of *soluble glass*. Boil the foil in water for a few minutes, filter; to a portion add excess of hydrochloric acid, evaporate the solution to dryness, and again boil the residue in water and acid; oxide of silicon, *silicic anhydride*, or *silica* (SiO_2), remains as a light, flaky, insoluble powder.

The *soluble glass* or *glass liquor* of trade commonly contains 10 or 12 per cent. of soda (NaHO) to 20 or 25 per cent. of silica (SiO_2). When of sp. gr. 1.300 to 1.400 it satisfies official requirements (*Liquor Sodii Silicatis*, U. S. P.).

The foregoing operation constitutes the *test* for silicates. By fusion with alkali the silicate is decomposed, and a soluble alkaline silicate formed. On addition of acid, silicic acid (H_4SiO_4) is set free, but remains in solution if sufficient water is present. The heat subsequently applied eliminates water and reduces the silicic acid to silica (SiO_2), which is insoluble in water or acid. By the addition of hydrochloric acid to soluble glass, and removal of the resulting alkaline chloride and excess of hydrochloric acid by dialysis (a process to be subsequently described), a pure aqueous solution of silicic acid may be obtained; it readily changes into a gelatinous mass of silicic acid. Possibly some of the natural crystallized varieties of silica may have been obtained from the silica contained in such an aqueous solution, nearly all waters yielding a small quantity of silica when treated as above described.

A variety of silicic acid (H_2SiO_3) sometimes termed *dibasic*, to distinguish it from the normal or *tetrabasic* acid (H_4SiO_4), results when the aqueous solution of the latter is evaporated *in vacuo*.

Siliciuretted hydrogen, or hydride of silicon (SiH_4), is a spontaneously inflammable gas formed on treating silicide of magnesium with hydrochloric acid. It is the analogue of light carburetted hydrogen (CH_4). A liquid chloride of silicon ($SiCl_4$) and a gaseous fluoride (SiF_4) also exist. Many other analogies are traceable between the elements silicon, boron, and carbon (see p. 330).

SUCCINIC ACID ($H_2C_4H_4O_4$).—Amber (*Succinum*) is a peculiar resin usually occurring in association with coal and lignite. From the fact that fragments of coniferous fruit are frequently found in amber, and impressions of bark on its surface, it is considered to have been an exudation from a species of *Pinus* now probably extinct. Heated in a retort, amber yields, first, a sour aqueous liquid containing acetic acid and another characteristic body appropriately termed *succinic acid;* second, a volatile liquid known as *oil of amber* (*Oleum Succini*, U. S. P.), resembling the oil yielded by most resinous substances under similar circumstances; and, third, a pitchy residue allied to asphalt. The succinic acid is a normal constituent of the amber; the acetic acid is produced during distillation. Succinic acid has also been found in wormwood, in several pine-resins, and in certain animal fluids, such as those of hydatid cysts, and hydrocele. It may be obtained artificially from butyric, stearic, or margaric acid by oxygen. Tartaric, malic, and succinic acids are also convertible the one into the other.

The *succinates* are normal ($R'_2C_4H_4O_4$) and acid ($R'HC_4H_4O_4$); a double succinate of potassium and hydrogen ($KHC_4H_4O_4.H_2C_4H_4O_4,H_2O$), analogous to the superacid oxalate, salt of sorrel, also exists.

Soluble succinates give a bulky brown precipitate with neutral ferric chloride, only less voluminous than ferric benzoate; a white precipitate with acetate of lead, soluble in excess of either reagent; with nitrate of silver, a white precipitate after a time; with chloride of barium, no precipitate at first, but a white one of succinate of barium on the addition of ammonia and alcohol. Succinates are distinguished from benzoates by the last-named reaction, and by not yielding a precipitate on the addition of acids (*vide* p. 334).

SULPHOCYANIC ACID (HCyS) AND OTHER SULPHOCYANATES.—Boil together sulphur and solution of cyanide of potassium; solution of sulphocyanate of potassium (KCyS) is formed. Warm the liquid, add hydrochloric acid till it faintly reddens litmus-paper, and filter; any sulphide of potassium is thus decomposed, and the solutions may then be used for the following reactions.

Tests.—Filter, and to a small portion of the solution add a ferric salt (Fe_2Cl_6); a deep blood-red solution of ferric sulphocyanate is formed. To a portion of the red liquid add a little hydrochloric acid; the color is not discharged (meconate of iron, a salt of similar tint, is decomposed by hydrochloric acid). In the acid liquid place a fragment or two of zinc; sulphuretted hydrogen is evolved, and the red color disappears. To another portion of the ferric sulphocyanate add solution of corrosive sublimate; the color is at once discharged. (Ferric meconate is unaffected by corrosive sublimate.) The ferric is the best test of the presence of a sulphocyanate; indirectly, it is a good test of the presence of hydrocyanic acid or cyanogen. Solutions of pure ferrous salts are not colored by the solution of sulphocyanate. Red ferric acetate is decomposed by ebullition.

Neither the ferric acetate nor the meconate yields its color to ether; but on shaking ferric sulphocyanate solutions with ether the latter takes up the salt and becomes of a purple color.

To solution of a sulphocyanate add solution of mercuric nitrate; mercuric sulphocyanate is precipitated as a white powder.

Pharaoh's Serpents.—Mercuric sulphocyanate, thoroughly washed and made up into little cones, forms the toy called Pharaoh's Serpent. It readily burns when ignited, the chief product being a light solid matter (mellon, C_9N_{13}, and the melam, $C_3H_6N_6$), which issues from the cone in a snake-like coil of extraordinary length. The other products are mercuric sulphide (of which part remains in the snake and part is volatilized), nitrogen, sulphurous, and carbonic acid gases, and vapor of metallic mercury. (For details concerning the economical manufacture of sulphocyanates, see *Pharmaceutical Journal*, second series, vol. vii. p. 581 and p. 152.)

The sulphocyanic radical (CyS) is often termed sulphocyanogen (Scy), and its compounds regarded as *sulphocyanides*. Saliva contains sulphocyanates.

TANNIC ACID, or TANNIN (*Acidum Tannicum*, U. S. P., $C_{14}H_{10}O_9$, chiefly).—This is a common astringent constituent of plants, but is contained in largest quantity in galls (excrescences on the oak formed by the puncture and deposited ova of an insect). English galls contain from 14 to 28 per cent. of tannic acid; Aleppo galls (*Galla*, U. S. P.) from 25 to 65 per cent. It is present also in the White Oak (*Quercus Alba*, U. S. P.).

Process.—" Expose powdered galls (about an ounce is sufficient for the purpose of study) to a damp atmosphere for two or three days, and afterward add sufficient ether to form a soft paste. Let this stand in a well-closed vessel for twenty-four hours; then, having quickly enveloped it in a linen cloth, submit it to strong pressure so as to separate the liquid portion, which contains the bulk of the tannin in solution. Reduce the pressed cake to powder, mix it with sufficient ether, to which one-sixteenth of its bulk of water has been added, to form again a soft paste, and press this as before. Mix the expressed liquids, and expose the mixture to spontaneous evaporation until, by the aid subsequently of a little heat, it has acquired the consistence of a soft extract; then place it on earthen plates or dishes and dry it in a hot-air chamber at a temperature not exceeding 212°."

The resulting tannic acid occurs in pale yellow vesicular masses or thin glistening scales, with a strongly astringent taste and an acid reaction, readily soluble in water and rectified spirit, very sparingly soluble in pure ether, though soluble in the ethereal fluid used in the foregoing process—a fluid which is really a mixture of true ether, water, and alcohol (both the latter contained in the common " ether "), and a little added water also.

Medicinal Uses.—Tannic acid is very soluble in water, and in this form is usually administered in medicine.

Tests.—To an aqueous solution of tannic acid add aqueous solution of gelatine; a yellowish-white flocculent compound of the two substances is precipitated. This is a good test of the presence of tannic acid.

Tanning.—The above reaction also serves to explain the chemical principle involved in *tanning*—the operation of converting skin into leather. In that process the skin is soaked in infusion of oak-bark (*Quercus cortex*), the tannic acid of which, uniting with the gelatinous tissues of the skin, yields a compound very well represented by the above precipitate. The outer bark of the oak contains little or no tannic acid, and is commonly shaved off from the pieces of bark which are large enough to handle; useless coloring-matter is thus also rejected. Other infusions and extracts besides that of oak-bark (chiefly catechu, sumach, and valonia) are largely used by tanners: if used alone these act too quickly, and give a harsh, hard, less-durable leather. The tannic acid of these preparations is probably slightly different from that of oak-bark.

To an aqueous solution of tannic acid add a neutral solution of a ferric salt; dark bluish-black tannate of iron is slowly precipitated. This is an excellent test for the presence of tannic acid in vegetable infusions. The precipitate is the basis of nearly all black writing-inks. Ferrous salts give at first only a slight reaction with tannic acid; but the liquid gradually darkens. Characters written with this liquid become quite black in a few hours, and are very permanent.

To an aqueous solution of tannic acid add solution of tartar-emetic; tannate of antimony is precipitated. This reaction and that with gelatin are useful in the quantitative estimation of the amount of tannic acid in various substances.

Tannic acid as it occurs in oak-bark is said to be a glucoside, that is, like several other substances, yields glucose (grape-sugar) when boiled with dilute sulphuric or hydrochloric acid, the other product being gallic acid.

Catechu, *Gambier*, or *Terra Japonica*, an extract of the *Uncaria Gambier;* as well as the true *Catechu*, *Cutch*, or *Terra Japonica*, an extract from the *Acacia catechu* (*Catechu*, U. S. P.; *Catechu nigrum*, P. I.) and *A. Suma; East Indian Kino* (*Kino*, U. S. P.) from the *Pterocarpus marsupium;* also *Bengal* or *Butea Kino*, from the *Palas* or *Dhak* tree, *Butea frondosa* (*Buteæ gummi vel Kino Bengalensis*, P. I.); *Elm-bark* (*Ulmi Cortex*, B. P.); and some other vegetable products, contain a variety of tannic acid (*mimotannic acid*), which gives a greenish precipitate with neutral solutions of ferric salts. According to Paul and Kingzett it yields, when decomposed, unfermentable sugar, and an acid different from ordinary gallic acid. Catechu and Gambier also contain *catechuic acid* or *catechin*, $C_{13}H_{12}O_5$, a body occurring in minute colorless acicular crystals, and, like mimotannic acid, affording a green precipitate with ferric salts.

Bael fruit (*Belæ Fructus*, B. P.), from the *Ægle Marmelos*, is said to owe its power as a remedy for dysentery and diarrhœa to a variety of tannic acid, but this is questionable. About 10 per cent. of tannic acid is contained in the leaves of *Castanea vesca* (*Castanea*, U. S. P.), the tree yielding the common edible Spanish chestnuts. The rind of the fruit of the *pomegranate* (*Punica granatum*) (*Granati Cortex*, P. I.) contains tannic acid. The astringency of Pomegranate-root Bark (*Granatum*, U. S. P.) is due to a tannic acid (its anthelmintic properties probably to a resinoid matter or possibly to what Tanret states to be a liquid alkaloid, *pellitierine*, $C_{16}H_{30}N_2O_2$). A tannic acid also probably gives the astringency to Logwood (*Hæmatoxylon*, U. S. P.), the *color* of which is due to oxidized *hæmatoxylin*. *Rhatany*-root bark (*Krameria*, U. S. P.) contains about 20 per cent. of tannic acid, its active astringent principle; rhubarb-root, about 9 per cent. *Bearberry*-leaves (*Uva Ursi*, U. S. P.) owe most of their therapeutic power to about 35 per cent. of tannic acid. (The cause of their influence on the kidneys is not yet traced.) They also contain *arbutin*, a crystalline glucoside. *Larch-bark* (*Laricis Cortex*, B. P.), the inner bark of *Pinus larix* or *Larix europæa*, contains, according to Stenhouse, a considerable amount of a tannic acid giving olive-green precipitates with salts of iron, and *larixin* and *larixinic acid* ($C_{10}H_{10}O_5$), a somewhat bitter substance. *Areca nuts* or *Betel nuts* (*Areca*, B. P.), from the Areca Palm (*Areca catechu*), contain, according to Flückiger and Hanbury, about 15 per cent. of "tannic matter." The extract of the fruit of *Gab*, or *Diospyros embryopteris* (*Diospyri Fructus*, P. I.), is a powerful astringent containing tannic acid. The rhizome (*Geranium*, U. S. P.) of *Geranium maculatum*, Spotted Cranesbill or Arum-root, contains both tannic and gallic acids. *Sumac* or *Shumac*, or *Sumach*, the leaves and stalks of various species of Rhus, chiefly *Rhus coriaria*, contains ordinary tannic acid and gallic acid. The fruit of sumach (*Rhus glabra*, U. S. P.) contains tannic and much malic acid. The bark of *Prinos verticillatus*, the *Black Alder* or *Winterberry* (*Prinos*, U. S. P.), contains tannin and a bitter principle. The principal constituent of the bark of the root of *Rubus villosus*, or *high blackberry*, and of *R. canadensis* and *R. trivialis* (*Rubus*, U. S. P.), is tannic acid.

Gallic Acid ($H_3C_7H_3O_5,H_2O$) (*Acidum Gallicum*, U. S. P.) occurs in small quantity in oak-galls and other vegetable substances, but is always prepared from tannic acid. Powdered galls are moistened with water and set aside in a warm place for five or six weeks, or until a little treated with water and filtered yields a solution which is only slightly precipitated with solution of isinglass, occasionally being remoistened; fermentation occurs, and impure gallic acid is formed. The product is treated with about three times its weight of water, boiled to dissolve the gallic acid, filtered, the solution set aside to cool, deposited gallic acid collected, drained, pressed between folds of paper to remove all mother-liquor, and, if necessary, purified by recrystallization from water, or by solution in hot water with animal charcoal, which absorbs coloring-matter. On filtering and cooling, most of the acid separates in the form of fawn-colored, slender acicular crystals. Gallic acid is soluble in about 100 times its weight of cold or 3 of boiling water, freely in spirit, sparingly in ether, also in glycerin.

The nature of the action by which gallic acid is thus produced is probably similar to that of the action of dilute acids on tannic acid. During the process oxygen is absorbed and carbonic acid gas evolved, the sugar being thus broken up or perhaps prevented from being formed.

Test.—To an aqueous solution of gallic acid add a neutral solution of ferric salt; a bluish-black precipitate of gallate of iron falls, similar in appearance to tannate of iron. Ferrous salts are also blackened by gallic acid. To more of the solution add an aqueous solution of gelatin; no precipitate occurs. By the latter test gallic acid is distinguished from tannic acid.

Pyrogallic Acid or *Pyrogallol* ($C_6H_6O_3$).—This substance sublimes in light feathery crystals when gallic acid is heated. Or it may be formed by heating gallic acid with 3 or 4 times its weight of glycerin to 190° or 200° C. for a short time until carbonic acid gas ceases to be evolved. Longer heating at a lower temperature is not equally effective, and below 100° C. probably no pyrogallol is produced (Thorpe). To an aqueous solution add a neutral solution of a ferric salt, a red color is produced. To another portion add a ferrous salt; a deep-blue color results.

Test for the Three Acids.—To three separate small quantities of milk of lime in test-tubes add, respectively, tannic, gallic, and pyrogallic acids; the first slowly turns brown, the second more rapidly, while the pyrogallic mixture at once assumes a beautiful purplish-red color, changing to brown. These reactions are highly characteristic. They are accompanied by absorption of oxygen from the air.

Use of Pyrogallic Acid in Gas-analysis.—A mixture of pyrogallic acid and solution of potash absorbs oxygen with such rapidity and completeness that a strong solution of each, passed up successively by a pipette into a graduated tube containing air or other gas, forms an excellent means of estimating free oxygen. The value of this method may be roughly proved by pouring a small quantity of each solution into a phial, immediately and firmly closing its mouth with a cork, thoroughly shaking the mixture, and then removing the cork under water; the water rushes in and occupies about one-fifth of the previous volume of air, indicating that the atmosphere contains one-fifth of its bulk of oxygen. The small amount of carbonic acid gas present in the air is also absorbed by the alkaline liquid; in delicate experiments this should be removed by the alkali before the addition of pyrogallic acid.

Toxicodendric Acid is the volatile, excessively acrid and poisonous principle of the Poison Oak or Poison Ivy, the fresh leaves of which are official (*Rhus toxicodendron*, U. S. P.), Maisch.

URIC ACID ($H_2C_5H_2N_4O_3$) AND OTHER URATES.—Acidulate a few ounces of human urine with hydrochloric acid, and set aside for twenty-four hours; a few minute crystals of uric acid will be found adhering to the sides and bottom of the vessel and floating on the surface of the liquid.

Microscopical Test.—Remove some of the floating particles by a slip of glass, and examine by a powerful lens or microscope; the chief portion will be found to be in yellowish semi-transparent crystals, more or less square, two of the sides of which are even, and two very jagged; but other forms are common (see the lithographs in the section on Urinary Sediments.)

Chemical Test.—Collect more of the deposit, place in a watch-glass or small white evaporating-dish, remove adherent moisture by a piece of blotting- or filter-paper, add a drop or two of strong nitric acid, and evaporate to dryness; the residue will be red. When the dish is cold add a drop of solution of ammonia; a purplish-crimson color results. The color is deepened on the addition of a drop of solution of potash.

Notes.—Uric acid (or lithic acid) and urates (or lithates) of sodium, potassium, calcium, and ammonium are common constituents of animal excretions. Human urine contains about one part of urate (usually urate of sodium) in 1000. When more than this is present the urate is often deposited as a sediment in the excreted urine, either at once or after standing a short time. Uric acid or other urate is also occasionally deposited before leaving the bladder, and, slowly accumulating there, forms a common variety of urinary calculus.——Some urates are not definitely crystalline; but when treated with dilute nitric acid or a drop of solution of potash, and then a drop or two of acetic acid, jagged microscopic crystals of uric acid are usually formed.—All urates yield the crimson color when treated as above described. This color is due to a definite substance *murexid* ($C_8H_8N_6O_6$) (from the *murex*, a shell-fish of similar tint); and the test is known as *the murexid test.* The formation of murexid is due to the action of ammonia on *alloxan* ($C_4H_2N_2O_4,4H_2O$) and other white crystalline products of the oxidation of uric acid by nitric acid. Murexid is a good dye; it may be prepared from *guano* (the excrement of sea-fowl), which contains a large quantity of urate of ammonium. The excrement of the serpent is almost pure ammonium urate.

Uric acid and the urates will be again alluded to in connection with the subject of morbid urine.

VALERIANIC ACID OR VALERIC ACID ($HC_5H_9O_2$) AND OTHER VALERIANATES.—In a test-tube place a few drops of amylic alcohol (fusel oil) with a little dilute sulphuric acid and a grain or two of red chromate of potassium, cork the tube, set aside for a few hours, and then heat the mixture; valerianic acid, of characteristic valerian-like odor, is evolved.

Valerianic acid occurs naturally in valerian-root in association with the essential oil from which it is derived (*vide* Index), but is usually prepared artificially, by the foregoing process, from amylic alcohol, to which it bears the same relation as acetic acid does to common alcohol:—

$$C_2H_5HO + O_2 = HC_2H_3O_2 + H_2O$$
$$C_5H_{11}HO + O_2 = HC_5H_9O_2 + H_2O.$$

Valerianate of Sodium ($NaC_5H_9O_2$) is prepared from the valerianic acid and valerianate of amyl obtained on distilling the mixture of amylic alcohol (4 fl. oz.), sulphuric acid (6½ fl. oz. with 10 of water), and red chromate of potassium (9 oz. in 70 of water). The mixture should stand for several hours before heat is applied.

$$\underset{\substack{\text{Red chromate of}\\\text{potassium.}}}{2(K_2CrO_4,CrO_3)} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{8H_2SO_4} = \underset{\substack{\text{Sulphate of potassium}\\\text{and chromium}\\\text{(Chrome alum).}}}{2(K_2SO_4,Cr_23SO_4)} + \underset{\text{Water.}}{8H_2O} + \underset{\substack{\text{Oxy-}\\\text{gen.}}}{3O_2}$$

$$\underset{\substack{\text{Amylic}\\\text{alcohol.}}}{C_5H_{11}HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Valerianic}\\\text{acid.}}}{HC_5H_9O_2} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\substack{\text{Amylic}\\\text{alcohol.}}}{2C_5H_{11}HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Valerianate}\\\text{of amyl.}}}{C_5H_{11}C_5H_9O_2} + \underset{\text{Water.}}{2H_2O}$$

The distillate (70 or 80 oz.) is saturated with soda, which not only yields valerianate of sodium with the free valerianic acid, but decomposes the valerianate of amyl produced at the same time, more valerianate of sodium being formed and some amylic alcohol set free, according to the following equations:—

$$\underset{\substack{\text{Valerianic}\\\text{acid.}}}{HC_5H_9O_2} + \underset{\text{Soda.}}{NaHO} = \underset{\substack{\text{Valerianate}\\\text{of sodium.}}}{NaC_5H_9O_2} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\substack{\text{Valerianate}\\\text{of amyl.}}}{C_5H_{11}C_5H_9O_2} + \underset{\text{Soda.}}{NaHO} = \underset{\substack{\text{Valerianate}\\\text{of sodium.}}}{NaC_5H_9O_2} + \underset{\substack{\text{Amylic}\\\text{alcohol.}}}{C_5H_{11}HO}$$

From the solution of valerianate of sodium (which should be made neutral to test-paper by careful addition of soda solution) the solid white salt is obtained by evaporation to dryness and cautious fusion of the residue. The mass obtained on cooling should be broken up and kept in a well-closed bottle. It is entirely soluble in spirit.

Other Valerianates, as valerianate of zinc (*Zinci Valerianas*, U. S. P.) and ferric valerianate (*Ferri Valerianas*, U. S. P.; $Fe_26C_5H_9O_2$), may be made by double decomposition of valerianate of sodium with the sulphate or other salt of the metal the valerianate of which is desired, the new valerianate either precipitating or crystallizing out. A hot solution of sulphate of zinc (5¾ parts) and valerianate of sodium (5 parts) in water (40 parts) gives a crop of crystals of valerianate of zinc on cooling.

Tests.—Heated with diluted sulphuric acid, valerianates of the metals give valerianic acid, which has a highly characteristic smell. Valerianate of sodium thus treated, and the resulting oily acid liquid purified by agitation with sulphuric acid and distillation, furnishes valerianic acid. Dry ammonia gas passed into valerianic acid gives white lamellar crystals of valerianate of ammonium (*Ammonii Valerianas*, U. S. P.).

The amylic alcohol ($C_5H_{11}HO$) from which valerianates are prepared may contain the next lower homologue, *butylic alcohol* (C_4H_9HO). This, during oxidation, will be converted into *butyric acid* ($HC_4H_7O_2$), the next lower homologue of valerianic acid ($HC_5H_9O_2$), and hence the various valerianates be contaminated by some *butyrates*. These are detected by distillation with diluted sulphuric acid and addition of solution of acetate of copper to the distillate, which at once becomes turbid if butyric acid be present. In this reaction valerianic and butyric acids are produced by double decomposition of the valerianate and butyrate by the sulphuric acid, and distil over on the application of heat. On the addition of acetate of copper ($Cu2C_2H_3O_2$) butyrate of copper ($Cu2C_4H_7O_2,H_2O$) is formed, and, being almost insoluble in water, is at once precipitated, or remains suspended, giving a bluish-white opalescent liquid. Valerianate of copper ($Cu2C_5H_9O_2$) is also formed after some time, but is far more soluble than the butyrate, and only slowly collects in the form of greenish oily drops, which gradually pass into greenish-blue hydrous crystalline valerianate of copper (Larocque and Huralt).

Vanillic Acid ($HC_8H_7O_3$) or Vanillin ($C_8H_8O_3$) or Methylprotocatechuic Aldehyd ($C_7H_5CH_3O_3$), the body to which is due the odor and flavor of Vanilla.—The white crystals commonly found on vanilla—the prepared unripe pods of *Vanilla planifolia*—previously termed *vanillin*, were found by Carles to be a weak acid. It occurs in vanilla to the extent of from 1½ to 3 per cent. Vanillin has recently been prepared artificially by Tiemann and Haarmann from coniferin, a glucoside existing in the sapwood of pines. The body remaining after the removal of glucose from coniferin, or, indeed, coniferin itself, by action of a mixture of red chromate of potassium and sulphuric acid, yields the vanillin. It also may be obtained by a series of reactions starting from that of carbonic acid on carbolate of potassium; also from the eugenol of oil of cloves. By action of hydrochloric acid, vanillin yields chloride of methyl and protocatechuic aldehyd. Such reactions will be better understood when the pupil has studied succeeding sections on what is commonly termed *Organic Chemistry*. Artificial vanillin is less stable than natural vanillin, perhaps because with the latter is associated a preservative resin.

QUESTIONS AND EXERCISES.

619. What is the constitution of nitrites?
620. Mention a test for nitrites in potable waters.
621. Which nitrite is official?
622. Give the names of some natural and artificial silicates.
623. What is "soluble glass"?
624. Distinguish between silica and silicic acid.

625. How are silicates detected?
626. What is the quantivalence of silicon?
627. Mention the sources, formulæ, and analytical reactions of succinates.
628. State the mode of manufacture and tests of sulphocyanates.
629. What proportion of tannic acid is contained in galls?
630. Describe a process for the preparation of Tannic Acid?
631. Explain the chemistry of "tanning."
632. Enumerate the tests of tannic acid.
633. What is the assumed constitution of tannic acid?
634. Mention official substances other than galls whose astringency is due to tannic acid.
635. How is gallic acid prepared?
636. By what reaction is gallic distinguished from tannic acid?
637. Mention the characteristic properties of pyrogallic acid.
638. Explain the murexid test for uric acid.
639. Describe the artificial preparation of valerianic acid and other valerianates, giving diagrams or equations.
640. What is the formula of valerianic acid?
641. How are butyrates detected in presence of valerianates?

DETECTION OF THE ACIDULOUS RADICALS OF SALTS SOLUBLE IN WATER.

Analytical operations may now be resumed, the detection of acidulous radicals being practised for two or three days, and then full analyses made, both for basylous and acidulous radicals. To this end a few compounds of stated metals (potassium, sodium, or ammonium) should be placed in the hands of the practical student for examination according to the following paragraphs and Tables. Mixtures in which both basylous and acidulous radicals may be sought should then be analyzed.

In examining salts soluble in water, and concerning which no general information is obtainable, search must first be made for any basylous radicals by the appropriate methods (*vide* page 219 or 255). Certain metals having been thus detected, a little reflection on the character of their salts will at once indicate what acidulous radicals may be, and what cannot be, present. Thus, for instance, if the substance under examination is freely soluble in water, and lead is found, only the nitric and acetic radicals need be sought, none other of the lead salts than nitrate or acetate being freely soluble in water. Moreover, the salt is more likely to be acetate than nitrate of lead, for two reasons: the former is more soluble than the latter, and is by far the commoner salt of the two. Medical and pharmaceutical students have probably, in dispensing, already learned much concerning the solubility of salts, and whether a salt is rarely employed or in common use. And although but little dependence can be placed on the chances of a salt being present or absent according to its rarity, still the point may have its proper weight. If, in a mixture of salts, ammonium, potassium, and magnesium have been found associated with the sulphuric, nitric, and hydrochloric radicals, and we are asked how we suppose these bodies may exist in the mixture, it is far more in accordance with common sense to suggest that sal-ammoniac, nitre, and Epsom salt were originally mixed together than to suppose any other possible combination. Such appeals to experience regarding the solubility or rarity of salts cannot be made by any one not previously acquainted, or insufficiently acquainted, with the characters of salts: in such cases the relation of a salt to water and acids can be ascertained by referring to the following Table (p. 363) of the solubility or insolubility of about five hundred of the common or rarer salts met with in chemical operations.

The opposite course to the above (namely, to ascertain what acidulous radicals are present in a mixture, and then to appeal to experience to tell what basylous radicals may be and what cannot be present) is impracticable; for acidulous radicals cannot be separated out, one after the other, from one and the same quantity of substance by a similar treatment to that already given for basylous radicals. Indeed, such a sifting of acidulous radicals could scarcely be accomplished at all, or only by a vast deal of labor. The basylous radicals must, therefore, be first detected.

Even when the basylous radicals have been found, the acidulous radicals which may be present must be sought for singly, the only additional aid which can be brought in being the action of sulphuric acid, a barium salt, a calcium salt, nitrate of silver, and ferric chloride on *separate* small portions of the solution under examination, as detailed in the second of the following Tables.

Commence the analysis of an aqueous solution of a salt or salts, the basylous radicals in which are known, by writing out a list of the acidulous radicals which may be, or, if more convenient, of those which cannot be, present. To this end consult the following Table (p. 363) of the solubility of salts in water. Look for the name of the metal of the salt in the vertical column; the letters S and I indicate which salts are soluble and which insoluble in water, an asterisk attached to the S meaning that the salt is slightly soluble. The acidulous part of the name is given in the top line of the Table. All the names are in alphabetical order, for facility of reference.

Some of the salts marked as insoluble in water are soluble in aqueous solutions of soluble salts, a few forming soluble double salts. To characterize salts as soluble, slightly soluble, or insoluble only roughly indicates their relation to water; on the one hand, very few salts are absolutely insoluble in water; on the other, there is a limit to the solubility of every salt.

If only one, two, or perhaps three, given acidulous radicals can be in the liquid, test directly for it or them according to the reactions given in the previous pages. If several may be present,

TABLE OF THE SOLUBILITY OR INSOLUBILITY OF SALTS IN WATER.

	Aeetate.	Arseniate.	Arsenite.	Carbonate.	Chloride.	Citrate.	Chromate.	Cyanide.	Hydrate.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Sulphate.	Sulphide.	Sulphite..	Tartrate.
Aluminium	S	I	I	I	S	S*	I	?	I	?	S	I	I	I	S	I	I	S
Ammonium	S	S	S	S	S	S	S	S	S	S	S	S	?	S	S	S	S	S
Antimony	S	I	I	?	S	?	I	?	I	I	?	S*	I	I	I	I	I	I
Barium	S	I	I	I	S	S*	I	S	S	S	S	I	S	I	I	S	I	I
Bismuth	S	I	?	I	S	S*	I	?	I	I	S	I	I	I	S	I	I	I
Cadmium	S	?	?	I	S	S*	?	?	I	S	S	I	I	I	S	I	S	S*
Calcium	S	I	I	I	S	S*	S	S	S*	S	S	I	S*	I	S*	S*	S*	S*
Chromium	S	I	?	I	S	S	I	I	I	S	S	S	I	I	S	I	S	S
Cobalt	S	I	I	I	S	S	?	I	I	S	S	I	I	I	S	I	S*	S
Copper	S	I	I	I	S	S	S	I	I		S	I	I	I	S	I	I	S*
Ferric	S	I	I	?	S	S	S	?	I	S	S	S*	I	I	S	I	?	S
Ferrous	S	I	I	I	S	S	?	I	I	S	S	S*	I	I	S	I	S*	S*
Gold	?	I	?	?	S	?	?	I	I	I	?	?	I	I	?	I	?	?
Lead	S	I	I	I	S*	S*	I	I	S*	S*	S	I	I	I	I	I	I	I
Magnesium	S	I	I	I	S	S	S	?	I	S	S	I	I	I	S	?	S	S
Manganese	S	I	?	I	S	I	S	I	I	S	S	I	I	I	S	I	S*	S*
Mercuric	S	I	I	I	S	?	S*	S	I	I	S	I	I	I	S	I	?	I
Mercurous	S*	I	I	I	I	I	I	?	?	I	S	I	I	I	S*	I	?	I
Nickel	S	I	I	I	S	S	I	I	I	S	S	I	I	I	S	I	S*	S*
Platinum	?	I	?	?	S	?	?	?	I	S*	S	?	I	?	S	I	S	?
Potassium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Silver	S*	I	I	I	I	I	I	I	?	I	S	I	I	I	S*	I	I	I
Sodium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Stannic	S	?	I	?	S	?	I	?	I	S	S	S	I	I	S	I	?	?
Stannous	S	I	I	?	S	?	I	?	I	S	S	I	I	I	S	I	I	S
Strontium	S	I	I	I	S	I	I	S	S	S	S	I	S	I	I	S	I	S*
Zinc	S	I	?	I	S	S*	S	I	?	S	S	I	I	I	S	I	S*	S*

TABLE TO AID IN THE DETECTION OF CHLORIDES, BROMIDES, IODIDES, CYANIDES, NITRATES, CHLORATES, BORATES, ACETATES, SULPHIDES, SULPHITES, SULPHATES, CARBONATES, OXALATES, TARTRATES, PHOSPHATES, AND CITRATES, IN A NEUTRAL AQUEOUS SOLUTION.

(For remarks concerning this Table see next page.)

Sulphuric Acid decomposes	**Chloride of Barium precipitates**	**Chloride of Calcium precipitates**	**Nitrate of Silver precipitates**	**Ferric Chloride precipitates**	**Not precipitated.**
Sulphides. Sulphites. Carbonates, with effervescence—hydrosulphuric and sulphurous acid gases, known by smell and carbonic acid gas, which has no special odor, being evolved. Cyanides, with production of the odor of hydrocyanic acid. Acetates, with production of the odor of acetic acid when the solution is warmed.	Borates. Sulphites. Sulphates. Carbonates.* Oxalates. Tartrates. Phosphates. Citrates. Of these white barium precipitates, the sulphate is the only one insoluble in hydrochloric acid; the tartrate and citrate char when heated on platinum foil; the sulphite and carbonate are decomposed with effervescence by acids.	Borates. Oxalates. Sulphites. Tartrates. Sulphates. Phosphates. Carbonates. Citrates. Of these white calcium precipitates, the sulphate only is sol. in much water; the borate, carbonate, and citrate are sol. in solution of chloride of ammonium: all are sol. in acetic acid except oxalate and some tartrate and sulphate; all are sol. in hydrochloric acid, much sulphate excepted; the dry tartrate and citrate char when heated; the sulphite and carbonate effervesce with acids.	Chlorides, white. Bromides, white. Iodides, yellow. Cyanides, white. Borates, white. Sulphides, black. Sulphates, white. Carbonates, white. Oxalates, white. Tartrates, white. Phosphates, yellow. Citrates, white. Of these silver precipitates, the chloride, bromide, iodide, cyanide, and sulphide are insoluble in dilute nitric acid; the rest soluble.	Borates, yellowish. Sulphides, black. Carbonates, reddish. Oxalates, yellow. Phosphates, yel.-white. Gives red color with acetates, if neutral.	Nitrates. Chlorates. Apply special tests.

Note.—The student should practise the examination of aqueous solutions of salts until able to detect acidulous radicals with facility and precision. For this purpose he may finish the analyses of salts or solutions already examined for common and rarer metals, or have aqueous solutions of salts, or the salts themselves, specially prepared for present use, the metals of the salts being stated. He will then be in a position to effectively study the analysis of salts which may or may not be soluble in water, examining them for both basylous and acidulous radicals.

* Bicarbonates are not precipitated by Chloride of Barium *in the cold.*

pour small portions of the solutions, rendered neutral if necessary by ammonia, into five test-tubes, and add respectively sulphuric acid, nitrate or chloride of barium, chloride of calcium, nitrate of silver, and ferric chloride; then consult the Table on page 364, in order to correctly interpret the effects these reagents may have produced.

REMARKS ON THE PRECEDING TABLE.

The first point of value to be noticed in connection with this Table is one of a negative character; namely, if either of the reagents gives no reaction, it is self-evident that the salts which it decomposes with production of a precipitate must be absent. Then, again, if the action of one of the reagents indicates the absence of certain acidulous radicals, those radicals cannot be precipitated by the other reagents; thus, if the action of sulphuric acid points to the absence of sulphides, sulphites, carbonates, cyanides, and acetates, these salts may be struck out of the other lists, and the examination of subsequent precipitates be so far simplified. Or, if the barium precipitate is soluble in hydrochloric acid and the calcium precipitate in acetic acid, neither sulphates nor oxalates can be present. Observing these and other points of difference, which will be seen on careful and thoughtful reflection, and remembering the facts suggested by a knowledge of what basylous radicals are present, one acidulous radical after the other may be struck off as absent or present, leaving only one or two as the objects of special experiment. Among the chief difficulties to be encountered will be the separation from each other of chlorides, bromides, iodides, and cyanides, or of tartrates from citrates, and confirmatory tests of the presence of certain compounds. These may all be surmounted on referring back to the reactions of the various radicals, as described under their hydrogen salts, the acids.

In rendering a solution neutral for the application of the various group-tests, the employment of any large amount of acid or of alkali must be noted; the presence of actual alkalies (that is, *hydrates*) or of acids, respectively, being thereby indicated.

Sulphuric acid, the first group-test, may itself yield, especially when heated with some solid substances, sulphurous acid or hydrosulphuric acid (see pp. 303 and 308); hence the production of the latter acids from a *diluted* solution only is evidence of the presence of a sulphide or sulphite.

In the precipitate produced by chloride of barium, the second group-test, the oxalic radical may be specially sought by the test described in the "note" on p. 314.

Chloride of calcium does not precipitate citrates readily or completely in the cold; therefore the mixture should be filtered and the filtrate boiled; calcium citrate then falls. Calcium tartrate is soluble in solution of chloride of ammonium when quite freshly precipitated, but not after it has become crystalline. From their solution in chloride of ammonium, tartrate of calcium is mostly precipitated by ammonia, and citrate on boiling.

The rarer acidulous radicals will very seldom be met with. *Ben-*

zoates, *hippurates* (which give benzoic acid), *hypochlorites*, *hyposulphites*, *nitrites*, and *valerianates* show themselves under the sulphuric treatment. *Ferrocyanides*, *ferridcyanides*, *meconates*, *succinates*, *sulphocyanates*, *tannates*, and *gallates* appear among the salts whose presence is indicated by ferric chloride; *formiates*, *hypophosphites*, *malates*, and others by nitrate of silver. *Urates* char when heated, giving an odor resembling that of burnt feathers.

In actual practice the analyst nearly always has some clue to the nature of rarer substances placed in his hands.

If chromium and arsenicum have been detected among the basylous radicals, those elements may be present in the form of *chromates*, *arseniates*, and *arsenites*, yielding with chloride of barium yellow chromate of barium and white arseniate and arsenite of barium, and with nitrate of silver, red chromate, brown arseniate, and yellow arsenite of silver.

QUESTIONS AND EXERCISES.

642. In analyzing an aqueous solution of salts, for which radicals would you first search, the basylous or the acidulous? and why?

643. In an aqueous solution there have been found magnesium (Mg) and potassium (K), with the sulphuric radical (SO_4) and iodine (I); state the nature of the salts which were originally dissolved in the water, and mention the principles which guide you in the conclusions.

644. Give a sketch of the method by which to analyze a neutral or only faintly acid aqueous liquid for the acidulous radical of salts. In what stage of the process would the following salts be detected?

a. Carbonates and Sulphates.
b. Oxalates.
c. Tartrates and Nitrates.
d. Acetates and Sulphites.
e. Bromides and Cyanides.
f. Borates.
g. Iodides and Phosphates.
h. Chlorates, Oxalates, and Acetates.
i. Chlorides and Iodides.
j. Sulphites.
k. Sulphides, Carbonates, and Nitrates.
l. Citrates and Sulphates.

645. Nitrate of silver gives no precipitate in an aqueous solution; what acidulous radicals may be present?

646. Chloride of barium gives no precipitate in a neutral solution, but nitrate of silver a white; what acidulous radicals are indicated?

647. Ferric chloride produces a deep-red color in a solution, chloride of calcium yielding no precipitate; what salts may be present? and how may they be distinguished from each other?

648. Ferric chloride gives a black precipitate in a solution in which sulphuric acid develops no odor; to what is the effect due?

ANALYSIS OF SALTS.

SINGLE OR MIXED, SOLUBLE OR INSOLUBLE.

Thus far, all material substances, especially those of pharmaceutical interest, have been regarded as being definite compounds, and as having certain well-defined parts, termed, for convenience, basylous and acidulous respectively; moreover, attention has been designedly restricted to those definite compounds which are soluble in water. But there are many substances having no definite or known composition; and of those having definite composition there are many having no definite or ascertained parts. Again, of those having definite composition, and whose constitution admits of the entertainment of theory, there are many insoluble in water.

Chemical substances of whose composition or constitution little or nothing is at present known, are chiefly of animal and vegetable origin, and figure in tables of analysis under the convenient collective title of "extractive matter;" they are not of immediate importance, and may be omitted.

Of substances which are definite in composition, but whose parts or radicals, if they have any, are unknown or imperfectly known, there are only a few (such as the alkaloids, amylaceous and saccharine matters, the glucosides, alcoholic bodies, albumenoid, fatty, resinoid, and colorific substances) which have any considerable amount of medical or pharmaceutical interest; these will be noticed subsequently.

Definite compounds most frequently present themselves; and of these by far the larger proportion (namely, the salts soluble in water) have already been fully studied. There remain, however, many salts which are insoluble in water, but which must be brought into a state of solution before they can be effectively examined from any analytical, pharmaceutical, or physiological point of view. The next subject of laboratory work is, therefore, the analysis of substances which may or may not be soluble in water. This will involve no other analytical schemes than those which have been given, will in only one or two cases increase the difficulty of the analysis of the precipitate produced by a group-reagent, but will give roundness, completeness, and a practical bearing to the reader's analytical knowledge. Such a procedure will at the same time bring into notice the methods by which substances insoluble in water are manipulated for pharmaceutical purposes, or made available for use as food by plants, or as food and medicine by man and animals generally.

Preliminary Examination of Solid (chiefly Mineral) Salts.

Before attempting to dissolve a salt for analysis, its appearance and other physical properties should be noted, and the influence of heat and strong sulphuric acid be ascertained. If the operator knows how to interpret what is thus observed, and to what extent to place confidence in the observations, he may more certainly obtain a high degree of precision in analysis, and will always gain some valuable negative information. But if he has only slight experience of the appearance and general properties of bodies, or has the habit of turning what should be inferences from tentative processes into foregone conclusions, he should omit the preliminary examination altogether, or only follow it out under the guidance of a judicious tutor; for it is impracticable here to do more than hint at the results which may be obtained by such an examination, or to so adapt description as to prevent a student from allowing unnecessary weight to preconceived ideas.

Whatever be the course pursued, short memoranda describing results should invariably be entered in the note-book.

1. Examine the physicial characters of the salt in various ways, but never, or only rarely, by the palate, on account of the danger to be apprehended.

If the salt is white, colored substances cannot be present; if colored, the tint may indicate the nature of the substance or of one of its constituents, supposing that the learner is already acquainted with the colors of salts. Closer observation, aided perhaps by a lens, may reveal the occurrence, in a pulverulent mixture, of small crystals or pieces of a single substance; these should be picked out by a needle and examined separately. In a powder or roughly divided mixture of substances, the process of sifting (through such sieves as muslin of different degrees of fineness) often mechanically separates substances, and thus greatly facilitates analysis. The body may present an undoubted metallic appearance, in which case only the metals existing under ordinary atmospheric conditions need be sought. Peculiarity in smell reveals the presence of ammonia, hydrocyanic acid, hydrosulphuric acid, etc. Between the fingers a substance is, perhaps, hard, soft, or gritty; consequent inferences follow. Or the matter may be heavy, like the salts of barium or lead; or light, like the carbonates and hydrates of magnesium; or may be one of the pharmaceutically well-known class of "scale" preparations.

2. Place a grain or two of the salt in a small dry test-tube or in a piece of ordinary tubing, closed at one end, and heat it, at first gently, then more strongly, and finally, if necessary, by the blowpipe.

Gases or vapors of characteristic appearance or odor may be evolved; such as iodine, nitrous fumes, sulphurous, hydrocyanic, or ammoniacal gases. Much steam given by a dry substance indicates either hydrates or salts containing water of crystallization. (A small quantity of interstitial moisture often causes heated crystalline substances to *decrepitate*—from *decrepo*, I crackle—that is, break up with slight explosive violence, owing to the expansive force of the steam suddenly generated). A sublimate may be obtained, due to salts of mercury or arsenicum, to oxalic or benzoic acid, or to sulphur free or as a sulphide—a salt wholly volatile containing such substances only. The compound may blacken, pointing to the presence of organic matter—which, in common definite salts, will probably be in the form of acetates, tartrates, and citrates, or as common salts of the alkaloids morphine, quinine, strychnine, or as starch, sugar, salicin, or in other definite or indefinite forms common in pharmacy and for which tests will be given in subsequent pages. If no charring occurs, the important fact that no organic matter is present is established. The residue may change color from presence or development of oxide of zinc, oxide of iron, etc., or melt from the presence of a fusible salt and absence of any large proportion of infusible salts. or, being unaltered, showing the absence of any large amount of such substances.

3. Place a grain or two of the salt in a test-tube, add a drop or two of strong sulphuric acid, cautiously smelling any gas that may be evolved; afterward slowly heat the mixture, noticing the effect, and stopping the experiment when any sulphuric fumes begin to escape.

Iodine, bromine, and nitrous or chlorinoid fumes will reveal themselves by their color, indicating the presence of iodides, bromides, iodates, bromates, nitrates, and chlorates. The evolution of a colorless gas fuming on coming into contact with air, and having an irritating odor, points to chlorides, fluorides, or nitrates. Gaseous products having a greenish color and odor of chlorine indicate chlorates, hypochlorites, or chlorides mixed with other substances. Slight sharp explosions betoken chlorates. Evolution of colorless gas may proceed from cyanides, acetates, sulphides, sulphites, carbonates, or oxalates. Charring will be due to citrates, tartrates, or other organic matter. If none of these effects are produced, most of the bodies are absent or only present in minute quantity. The substances apparently unaffected by the treatment are metallic oxides, borates, sulphates, and phosphates.

4. Exposure of the substances to the blowpipe-flame, on platinum wire with or without a bead of borax or microcosmic salt (phosphate of sodium, ammonium, and hydrogen, $NaAmHPO_4$) —on platinum foil, in a porcelain crucible, or on a crucible-lid with or without carbonate of sodium—on charcoal, alone or in conjunction with carbonate of sodium, cyanide of potassium, or nitrate of cobalt, will sometimes yield important information, especially to one who has devoted much attention to reactions produceable by the blowpipe-flame. The medical or pharmaceutical student, however, will seldom have time to work out this subject to an extent sufficient to make it a trustworthy guide in analysis. (See Plattner and Muspratt *On the Use of the Blowpipe*, and a chapter in Galloway's *Manual of Quantitative Analysis*.

Methods of Dissolving and Analyzing Single or Mixed Solid Substances.

Having submitted the substance to preliminary examination, proceed to dissolve and analyze by the following methods. These operations consist in treating a well-powdered substance consecutively with cold or hot water, hydrochloric acid, nitric acid, nitro-hydrochloric acid, or fusion with alkaline carbonates and solution of the product in water and acid. Resulting liquids are analyzed in the manner already described, or by slightly modified processes as detailed in the following paragraphs.

Solution in Water.—Boil about a grain of the salt presented for analysis in about a third of a test-tubeful of water. If it dissolves, prepare a solution of about 20 or 30 grains in half an ounce or more of water, and *proceed with the analysis in the usual way*, testing first for the basylous radical or radicals by the proper group reagents (HCl, H_2S, $AmHS$, Am_2CO_3, Am_2HPO_4), p. 220 or 255, and then for the acidulous radical or radicals, directly or by aid of the prescribed reagents (H_2SO_4, $BaCl_2$, $CaCl_2$, $AgNO_3$, Fe_2Cl_6), p. 364.

If the salt is not *wholly* dissolved by the water, ascertain whether or not any has entered into solution, by filtering, if necessary, and evaporating a drop or two of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought. If anything is dissolved, prepare a sufficient quantity of solution for analysis and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with water, for subsequent treatment by acids.

Solution in Hydrochloric Acid.—If the salt is insoluble in water, digest about a grain of it (or of the insoluble portion of a mixed salt) in a few drops of hydrochloric acid, adding water, and boiling if necessary. If the salt wholly dissolves, prepare a sufficient quantity of the liquid, noticing whether or not any effervescence (due to the presence of sulphides, sulphites, carbonates, or cyanides) occurs, and proceed with the analysis as before, except that the first step, the addition of hydrochloric acid, may be omitted.

The analysis of this solution will in most respects be simpler than that of an aqueous solution, inasmuch as the majority of salts (all those soluble in water) will be absent. This acid solution will, in short, only contain: chlorides produced by the action of the hydrochloric acid on sulphides, sulphites, carbonates, cyanides, oxides, and hydrates; and certain borates, oxalates, phosphates, tartrates, and citrates (possibly silicates and fluorides) which are insoluble in water, but soluble in acids without apparent decomposition. The first four—sulphides, sulphites, carbonates, and cyanides—will have revealed themselves by the occurrence of effervescence during solution; and the presence of oxides and hydrates may often be inferred by the absence of compatible acidulous radicals. The borates, oxalates, phosphates, tartrates, and citrates alluded to will be reprecipitated in the general analysis as soon as the acid of the solution is neutralized; that is, will come down in their original state when ammonia and sulphydrate of ammonium are added to the usual course. Of these precipitates, only the oxalate of calcium and the phosphates of calcium and magnesium need occupy attention now; for oxalate and phosphate of barium seldom or never occur, and the borates, tartrates, and citrates met with in medicine or in general analysis are all soluble in water. These phosphates and oxalates, then, will be precipitated in the course of analysis along with iron, their presence not interfering with the detection of any other metal. If, from the unusual light color of the ferric precipitate, phosphates and oxalates are suspected, it is treated according to the following Table (reference to which should be inserted in the Table for metals, under Fe, pp. 220 and 255).

PRECIPITATE OF PHOSPHATES, OXALATES, AND FERRIC HYDRATE.

Dissolve in HCl, add citric acid, then NH_4HO, and filter.

<table>
<tr>
<td rowspan="3">Filtrate
Fe.
Add HCl and
K_4Fey.
Blue ppt.</td>
<td colspan="3">Precipitate
Ca_32PO_4, CaC_2O_4, Mg_32PO_4.
Boil in acetic acid and filter.</td>
</tr>
<tr>
<td rowspan="2">Insoluble
CaC_2O_4.*
White.
(CaF_2 *may* occur here.)</td>
<td colspan="2">Filtrate
Ca_32PO_4, Mg_32PO_4.
Add $Am_2C_2O_4$, stir, filter.</td>
</tr>
<tr>
<td>Precipitate
white, including
Ca_22PO_3.</td>
<td>Filtrate.
Add AmHO.
White ppt.
$MgNH_4PO_4$.</td>
</tr>
</table>

In analyzing phosphates and oxalates advantage is also frequently taken of the facts that the phosphoric radical is wholly removed from solution of phosphates in acid by the addition of an alkaline acetate, ferric chloride, and subsequent ebullition, as described under "Phosphoric Acid" (p. 328), and that dry oxalates are converted into carbonates by heat, as mentioned under "Oxalic Acid" (p. 314). See also p. 328, 4th Analytical Reaction.

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* Oxalates after being heated effervesce on the addition of acid; fluorides may be detected by the "etching test."

Certain arseniates and arsenites, insoluble in water but soluble in hydrochloric acid, may accompany the above phosphates and oxalates if from any cause hydrosulphuric acid gas has not been previously passed through the solution, or passed for an insufficient length of time.

If the substance insoluble in water does not *wholly* dissolve in hydrochloric acid, ascertain if any has entered into solution, by filtering, if necessary, and evaporating a drop of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought. If anything is dissolved, prepare a sufficient quantity of solution for analysis, and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with hydrochloric acid and well washing with water, for the following treatment by nitric acid.

Solution in Nitric Acid.—If the salt is insoluble in water and hydrochloric acid, boil it (or that part of it which is insoluble in those menstrua) in a few drops of nitric acid. If it wholly dissolves, remove excess of acid by evaporation, dilute with water, and proceed with the analysis.

This nitric solution can contain only very few substances: for nearly all salts soluble in nitric acid are also soluble in hydrochloric acid, and therefore will have been removed previously. Some of the metals, however (Ag, Cu, Hg, Pb, Bi), as well as amalgams and alloys, unaffected or scarcely affected by hydrochloric acid, are readily attacked and dissolved by nitric acid. Many of the sulphides, also insoluble in hydrochloric acid, are dissolved by nitric acid, usually with separation of sulphur. Calomel is converted, by long boiling with nitric acid, into mercuric chloride and nitrate. The nitrates here produced are soluble in water.

This nitric solution, as well as the hydrochloric and aqueous solutions, should be examined separately. Apparently time would be saved by mixing the three solutions together and making one analysis. But the object of the analyst is to separate every radical from every other; and when this has been partially accomplished by solvents, it would be unwise to again mix and separate a second time. Moreover, solvents often do what the chemical reagents cannot—namely, separate *salts* from each other. This is important, inasmuch as the end to be obtained in an analysis is not only an enumeration of the radicals present, but a statement of the actual condition in which they are present; the analyst must, if possible, state of what salts a given mixture was originally formed—how the basylous and acidulous radicals were originally distributed. In attempting this, much must be left to theoretical considerations; but a process by which the salts themselves are separated is of trustworthy practical assistance; hence the chief advantage of analyzing separately the solutions resulting from the action of water and acids on a solid substance.

Solution in Nitro-Hydrochloric Acid.—If the salt or any part of a mixture of salts is insoluble in water, hydrochloric acid, and nitric acid, digest it in nitro-hydrochloric acid, warming or even boiling gently if necessary; evaporate to remove excess of acid, dilute, and proceed as before.

Sulphide of mercury and substances only slowly attacked by hydrochloric or nitric acid, as, for example, calomel and ignited ferric oxide, are sufficiently altered by the free chlorine of aqua regia to become soluble.

Analysis of Insoluble Substances.

If the substance is insoluble in water and acids, it is one or more of the following substances: Sand and certain silicates, such as pipeclay and other clays; fluor spar; cryolite ($3NaF,AlF_3$); sulphates of barium, strontium, and possibly calcium; tinstone; antimonic oxide; glass; felspar (double silicate of aluminium and other metals); chloride of silver; sulphate of lead. It may also be or contain carbon or carbonaceous matter, in which case it is black and combustible, burning entirely or partially away when heated in the air; or be or contain sulphur, in which case sulphurous gas is evolved, detected by its odor, when the substance is heated in the air. A drop of solution of sulphydrate of ammonium added to a little of the powder, will at once indicate the presence or absence of salts of such metals as lead and silver. For the other substances proceed according to the following (Bloxam's) method:—

Four or five grains of the dry substance are intimately mixed with twice the quantity of dry carbonate of sodium, and this mixture well rubbed in a mortar with five times its weight of *deflagrating flux* (1 of finely-powdered charcoal to 6 of nitre). The resulting powder is placed in a thin porcelain dish, or crucible, or clean iron tray, and a lighted match applied to the centre of the heap. Deflagration ensues, and decomposition of the various substances occurs, the acidulous radicals going to the alkali-metals to form salts soluble in water, the basylous radicals being simultaneously converted into carbonates or oxides. The mass is boiled in water for a few minutes, the mixture filtered, and the residue well washed. The filtrate may then be examined for acidulous radicals and aluminium, and the residue dissolved in dilute hydrochloric acid and analyzed by the ordinary method.

The only substance which resists this treatment is chrome-iron ore.

To detect alkali in felspar, glass, or cryolite, Bloxam recommends deflagration of the powdered mineral with one part of sulphur and six of nitrate of barium. The mass is boiled in water, the mixture filtered, hydrate and carbonate of ammonium added to remove barium, the mixture again filtered, and the filtrate evaporated and examined for alkalies by the usual process.

Hydrates and Oxides.

If no acidulous radical can be detected in a substance under analytical examination, or if the amount found is obviously insufficient to saturate the quantity of basylous radical present, the occurrence of oxides or hydrates, or both, may be suspected. Confirmation of their presence will be found in the general rather than in any special behavior of the substances. Some hydrates yield water when heated—in a dry test-tube held nearly horizontally in a flame, so that moisture may condense on the cool part of the tube. Some oxides yield oxygen—detected by heating in a test-tube, and inserting the incandescent end of a strip of wood. Soluble hydrates cause abundant evolution of ammonia gas when heated with solution of chloride of ammonium. Soluble hydrates also give characteristic precipitates with the various metallic solutions. Hydrates and oxides insoluble in water not only neutralize much nitric acid or acetic acid, but are thereby converted into salts soluble in water. Most oxides and hydrates have a characteristic appearance. In short, some one or more properties of an oxide or a hydrate will generally betray its presence to the student who not only has knowledge respecting chemical substances, but has cultivated the faculties of observation and perception.

QUESTIONS AND EXERCISES.

649. Describe the preliminary treatment to which a salt may be subjected prior to systematic analysis.

650. Mention substances which might be recognized by smell.

651. Which classes of salts are heavy, and which light?

652. Name some bodies detectable by their color.

653. What inference may be drawn from the appearance of steam when dry substances are heated?

654. Why do certain crystals decrepitate?

655. If a powder sublimes on being heated, to what classes of compounds may it belong?

656. When heat causes charring, what conclusion is drawn?

657. No change occurring by heat, which substances cannot be present?

658. Give example of salts which are identified by their reaction with strong sulphuric acid; and by their comportment in the blowpipe-flame, with or without borax or microcosmic salt.

659. What are the solvents usually employed in endeavoring to

obtain a substance in a state of solution, and what is the order of their application?

660. Name a few salts which may be present in an aqueous solution.

661. Mention some common compounds insoluble in water, but soluble in hydrochloric acid.

662. What substances are attacked only by nitric acid or nitrohydrochloric acid?

663. At what stage of analysis do arsenites and arseniates show themselves?

664. Sketch out a method for the complete analysis of a liquid suspected to be an aqueous solution of neutral salts.

665. How can earthy phosphates and oxalates with ferric oxide be separated from each other?

666. How would you proceed to analyze an alloy?

667. By what process may substances insoluble in water or acids be analyzed?

668. How would you qualitatively analyze glass?

RECAPITULATORY AND OTHER NOTES ON THE CONSTITUTION OF THE DEFINITE CHEMICAL COMPOUNDS COMMONLY TERMED SALTS.

The molecules of a salt contain radicals—which may be either elementary or compound: pp. 37 and 66.

Each radical has a definite exchangeable value: p. 120.

The definite exchangeable values of radicals differ in different series of radicals: p. 121.

In one and the same molecule of a salt, two or more different atoms of the same element may possess the two distinct functions of being (*a*) a single definite distinct radical and (*b*) one member of a group of atoms which together form a single definite distinct radical: p. 260.

The relation to each other, either of the elementary or the compound radicals in organic substances or salts, is apparently far more complex than the relation to each other of the elementary and compound radicals in inorganic or mineral salts: pp. 377 and 378.

The properties of salts are regarded as depending on (*a*) the nature, (*b*) the number, and (*c*) the position in relation to each other of the elementary and compound radicals in a molecule.

Dumas, afterwards Laurent, and then Gerhard, attempted the classification of salts under such *types* as the following:—

$$\left.\begin{matrix}H\\H\end{matrix}\right\} \qquad\qquad \left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad\qquad \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$$

The hydrogen type. The water type. The ammonia type.

Other chemists have extended the number of such types of salts. Further, by writing the typical formulæ in the above and other manners a mode of indicating the facts assumed to be dependent on the position of the atoms in a molecule has been sought to be obtained.

Finally, the natural development of this train of thought and of practice has produced the *graphic formulæ* of Kékulé, Frankland, and others.

Caution.—The conjectural or theoretic character of our ideas respecting masses of matter being formed of molecules, and molecules of atoms, and that molecules contain radicals consisting of one or more atoms, must never be lost sight of—highly valuable and practically useful though the hypotheses be: pp. 38, 50, 260, 261, 283, 299.

Berthollet's Laws.—"When we cause two salts to react by means of a solvent, if, in the course of double decomposition, a new salt can be produced less soluble than those which we have mixed, this salt will be produced. When we apply dry heat to two salts, if, by double decomposition, a new salt can be produced more volatile than the salts previously mixed, this salt will be produced."

Malaguti's Law.—When solutions of two different salts are mixed, and metathesis occurs and four salts result, the proportions of the salts to each other are dependent on the strength or intensity of force with which the respective basylous and acidulous radicals are united.

The state of equilibrium just mentioned may be permanent or temporary. The latter condition obtains when one of the salts which may possibly be produced is insoluble, for as soon as precipitation occurs the equilibrium is upset, and is re-established only to be upset again, and so on until from the four salts there result one in solution and one out of solution. This would seem to be the way in which the laws termed Berthollet's work.

CHEMISTRY OF CERTAIN SUBSTANCES OF VEGETABLE AND ANIMAL ORIGIN.

Except alcohol and a few acids, the compounds which have hitherto engaged notice have been of mineral origin. But the two other kingdoms of nature, the animal and vegetable, furnish a large number of definite substances. These, indeed, when discovered, were producible only by organized living structures, and were hence termed *organic* compounds.*

A few of these compounds of common occurrence in pharmacy, and possessing prominent characteristics, may now occupy attention; reactions of the alkaloids and some other principles may be performed, and the methods of examining morbid urine be experimentally studied. There will then remain to be studied certain galenical, as distinguished from chemical, substances, solid and liquid, which can only be fairly regarded from a pharmacist's rather than a chemist's point of view, and a still larger number, doubtless, not yet brought within the grasp of chemist or pharmacist, and of which, therefore, we must at present be content to remain in ignorance. An opportunity, however, will be afforded of noticing the effect of such organic matter as a vomit or the contents of a stomach in masking or preventing the reactions by which mineral and vegetable poisons are detected.

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* *Organic*, from ὄργανον, *organon*, an organ. A large number of organic compounds can now be obtained artificially—without the aid of a living organism; hence the distinction formerly drawn between organic and inorganic compounds, organic and inorganic chemistry, is fast breaking down.

ALKALOIDS.

Constitution of Alkaloids or Organic Bases.

Natural Alkaloids.—The alkaloids, or alkali-like bodies (*εἶδος*, *eidos*, likeness), have many analogies with ammonia. Their constitution is not yet known; but they are probably derivatives of a single molecule of ammonia (NH_3), or of double, triple, or quadruple molecules (N_2H_6, N_3H_9, N_4H_{12}).

Artificial Alkaloids.—Numerous artificial alkaloids or organic bases, unquestionably having the constitution just mentioned, have already been formed. These are sometimes termed *amines*, and are primary, secondary, and tertiary, according as one, two, or three atoms of hydrogen in ammonia have been displaced by radicals, as seen in the following general formulæ (R = any univalent radical. *Vide* Index, "Alcohol Radicals"):—

$$\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N \qquad\qquad \left.\begin{matrix}R\\R\\H\end{matrix}\right\}N \qquad\qquad \left.\begin{matrix}R\\R\\R\end{matrix}\right\}N$$

or the following examples:—

$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N \qquad\qquad \left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N \qquad\qquad \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$$

Ethylamine or ethylia (C_2H_7N).	Diethylamine or diethylia ($C_4H_{11}N$).	Triethylamine or triethylia ($C_6H_{15}N$).

The three classes have also been termed amidogen-, imidogen-, and nitrile-bases.

Mode of Formation of Artificial Alkaloids.—A few illustrations will suffice. Just as the addition of iodide of hydrogen (HI) to ammonia (that is, the common tri-hydrogen ammonia, NH_3) gives iodide of common ammonium (NHHHHI or NH_4I), so the addition of iodide of ethyl (C_2H_5I or EtI) (see Index) to ammonia (NH_3) gives the iodide of ethyl-ammonium (NHHHEtI, or NH_3EtI, or $NH_3C_2H_5I$). A fixed alkali turns out common *ammonia* (NHHH) from the iodide (or any other salt) of common ammonium; it turns out ethyl-ammonia (NHHEt) from the iodide (or any other salt) of ethyl-ammonium. Ethyl-ammonia (or *ethylia*, or ethylamine), NHHEt, with iodide of ethyl, EtI, gives iodide of diethyl-ammonium (NHHEtEtI, or NH_2Et_2I, or $NH_2[C_2H_5]_2I$). From the latter, potash turns out diethyl-ammonia ($NHEt_2$); diethyl-ammonia (*diethylia* or diethylamine) with iodide of ethyl gives iodide of triethyl-ammonium ($NHEt_3I$). The latter with alkali gives triethyl-ammonia or *triethylia* or triethylamine (NEt_3), and this with iodide of ethyl gives iodide of tetrethyl-ammonium, NEt_4I.

What has just been stated respecting iodide of ethyl is true of other salts of ethyl; and what is true of salts of ethyl is true of salts of an immense number of other radicals—univalent, bivalent, etc.—so that a vast number of artificial alkaloids and their salts can be produced. The reactions are not always so sharp as those just given. Mixtures of primary, secondary, and tertiary compounds rather than either alone often result in an experiment; but the reactions are typically true.

Some of these artificial alkaloids not only resemble natural alkaloids, but are strong caustic liquids, like solution of ammonia.

Then, the displacing radical in an artificial alkaloid or its salt may not only be of one kind, as indicated in the preceding paragraphs, but of different kinds; and while the radical displacing one atom of hydrogen is keeping its place, any of the many known radicals may occupy the position of one or all of the other atoms of hydrogen. Thus, for example, we have methyl-ethyl-amyl-amine ($C_8H_{19}N$, or $CH_3C_2H_5C_5H_{11}N$, or MeEtAyN), a colorless oily body, of agreeable aromatic odor. The empirical formulæ of morphine, quinine, etc. may some day be similarly resolvable into rational formulæ. Their artificial production will then quickly follow.

Methylamine (CH_3HHN), and *trimethylamine* ($(CH_3)_3N$, are artificial alkaloids which have been found by Schmidt in *Mercurialis annua* and *M. perennis*, and previously by Reichardt, who termed them *mercurialine*. Trimethylamine is also produced in large quantities in the dry distillation of the evaporated residue of the spent wash produced in beet-root spirit distilleries.

Propylamine or *tritylia* (C_3H_7HHN) is a volatile oil, one product of the destructive distillation of bones and other animal matters.

The organic bases derived from one molecule of ammonia are termed monamines; from two molecules, diamines; from three, triamines; and from four, tetramines:—

$$\left.\begin{matrix}R\\R\\R\end{matrix}\right\}N \qquad \left.\begin{matrix}R_2\\R_2\\R_2\end{matrix}\right\}N_2 \qquad \left.\begin{matrix}R_3\\R_3\\R_3\end{matrix}\right\}N_3 \qquad \left.\begin{matrix}R_4\\R_4\\R_4\end{matrix}\right\}N_4$$

In these amines any bivalent, trivalent, or quadrivalent radical may occupy the place of two, three, or four univalent radicals.

Evidence of Constitution of the Natural Alkaloids.—Attempts to form artificially the important natural organic bases have hitherto failed; but the primary, secondary, or tertiary character of some of them has been indicated by the introduction or elimination of methyl, ethyl, and other radicals for hydrogen.

Note on Nomenclature of Natural Alkaloids.—The first syllables of the names of the natural alkaloids recall the name of the plant whence they were obtained or some characteristic property. It is to be regretted that the last syllable is not either *ine* or *ia*, instead of sometimes one and sometimes the other. In the United States the termination *ine* is officially adopted, although the termination *ia* is still frequently employed. The names of the salts of the alkaloids are given on the assumption that the acid unites with the alkaloid without decomposition. Thus hydrochlorate of morphine is regarded as morphine with hydrochloric acid, just as we might assume sal-ammoniac to be ammonia (NH_3) with hydrochloric acid (HCl), and name it hydrochlorate of ammonia (NH_3HCl) instead of chloride of ammonium (NH_4Cl). All acids, even sulphydric, unite with alkaloids and form salts having similar names.

Antidotes.—In cases of poisoning by alkaloids, emetics and the stomach-pump must be relied on rather than chemical agents. But astringent liquids may be administered, for tannic acid precipitates many of the alkaloids from their aqueous solution, absorption of the poison being thus possibly retarded.

MORPHINE, OR MORPHIA.

Formula $C_{17}H_{19}NO_3,H_2O$. Molecular weight 303.

Occurrence.—Morphine occurs in opium (the inspissated juice of the fruit, *Papaveris capsulæ*, of the White Poppy, *Papaver somniferum*) as meconate of morphine [$(C_{17}H_{19}NO_3)_2$, $C_7H_4O_7$, $5H_2O$; Dott.]. The dried poppy-capsule of pharmacy contains opium principles, but varying much in nature and proportion. The presence in the capsule of morphine, narcotine, and meconic acid have been demonstrated, and, by Groves, of narceine and codeine. Ordinary Asia Minor opium (*Opium*, U. S. P.) (Turkey, Smyrna, or Constantinople opium) should contain "not less than 9 per cent. of morphine," and when dried at 85° C. and powdered (*Opii Pulvis*, U. S. P.), from 12 to 16 per cent. of morphine.

Denarcotized Opium (*Opium Denarcotisatum*, U. S. P.) is dried and powdered opium from which narcotine has been washed out by ten times its weight of stronger ether, the product being re-dried at 85° C., and made up to its original weight with powdered sugar of milk.

Morphina, U. S. P., may be made by adding to infusion of opium an equal bulk of alcohol, then slight excess of ammonia, and setting aside for crystalline morphine to separate. It is purified by recrystallization.

Process for Hydrochlorate.—The hydrochlorate, $C_{17}H_{19}NO_3,HCl,3H_2O$ (*Morphinæ Hydrochloras*, U. S. P.), occurs in slender white acicular crystals. It is prepared by simply decomposing an aqueous infusion of opium with chloride of calcium, meconate of calcium and hydrochlorate of morphine being produced. (If the infusion, which is always acid, be first nearly neutralized by the cautious addition of small quantities of very dilute solution of ammonia, the chloride of calcium then at once causes a precipitate of meconate of calcium, which can be filtered off, leaving a colored solution of hydrochlorate of morphine. On the large scale (*vide* B. P.) the details are somewhat different.) The salt is partially purified by crystallization from the evaporated liquid, then by treatment of the solution of the impure hydrochlorate by animal charcoal, and lastly, by precipitation of the morphine from the still colored liquid by ammonia and re-solution of the morphine in hot dilute hydrochloric acid; hydrochlorate of morphine separates out on cooling.

Hydrochlorate of morphine deposited from a hot solution in about twenty times its weight of alcohol is anhydrous.

Morphine may also, of course, be prepared by the methods given for its quantitative separation from opium (see Index).

Morphinæ Sulphas, U. S. P. ($2C_{17}H_{19}NO_3,H_2SO_4,5H_2O$) may be made by neutralizing morphine with sulphuric acid. It is a constituent of *Pulvis Morphinæ Compositus*.

Process for Acetate.—Acetate of morphine ($C_{17}H_{19}NO_3,C_2H_4O_2$) (*Morphinæ Acetas*, U. S. P.) is a white pulverulent salt prepared by dissolving pure morphine in acetic acid. One grain of acetate, so made, in twelve minims of water, forms the *Injectio Morphiæ Hypodermica*, B. P.

Both the hydrochlorate and acetate of morphine are soluble in water, but the solution is not stable unless acidulated and containing alcohol; hence the official solutions, 4 grains in one ounce, 1 in 110 (*Liquor Morphiæ Hydrochloratis*, B. P., and *Liquor Morphiæ Acetatis*, B. P.), consist of three parts water and one part rectified spirit, a few minims per ounce of hydrochloric or acetic acid being added. Even solid acetate of morphine is unstable, slowly dissociating into acetic acid and morphine; hence the acid odor of acetate of morphine.

Solubility of morphine salts in water at 60° F. According to Dott, 1 part of the respective salts is soluble in the annexed number of parts of water: Acetate, 2½; Tartrate, 9¾; Sulphate, 23; Hydrochlorate, 24; Meconate, 34.

Other alkaloids exist in opium. In the above process a considerable quantity of an alkaloid of very weak basic properties, *narcotine* ($C_{22}H_{23}NO_7$) (*Narcotina*, P. I.) remains in the exhausted opium, and may be extracted by digesting in acetic acid, filtering, precipitating by ammonia. It crystallizes in brilliant needles from alcohol or ether. By oxidation it yields *cotarnine* and an acid termed *opianic*. *Codeine* ($C_{18}H_{21}NO_3,H_2O$) (*Codeina*, U. S. P.) is soluble in the slight excess of ammonia employed in precipitating the morphine. "Codeine is dissolved by sulphuric acid containing 1 per cent. of molybdate of sodium to a liquid having, at first, a dirty-green color, which, after a while, becomes pure blue, and gradually fades, within a few hours, to pale yellow. On dissolving codeine in sulphuric acid a colorless liquid results, which, on the addition of a trace of ferric chloride and gentle warming, becomes deep blue. An aqueous solution of codeine, added to test-solution of mercuric chloride, should produce no precipitate; and if codeine be added to nitric acid of sp. gr. 1.200, it will dissolve to a yellow liquid which should not become red (difference from and abs. of morphine)."—U. S. P. From the mother-liquors there have also been obtained *thebaine* ($C_{19}H_{21}NO_3$), *papaverine* ($C_{21}H_{21}NO_4$), *opianine* ($C_{21}H_{21}NO_7$?), *narceine* ($C_{23}H_{29}NO_9$), *cryptopine* ($C_{21}H_{23}NO_5$), *meconine* ($C_{10}H_{10}O$), *meconoisine* ($C_8H_{10}O_2$), *landanine* ($C_{20}H_{23}NO_4$), *codamine* ($C_{20}H_{25}NO_4$), *gnoscopine* ($C_{34}H_{36}$-

N_2O_{11}), *pseudomorphine* ($C_{17}H_{19}NO_4$), *protopine* ($C_{20}H_{19}NO_5$), *laudanosine* ($C_{21}H_{27}NO_4$), *hydrocotarnine* ($C_{12}H_{15}NO_3$), *rhœadine* ($C_{20}H_{21}NO_6$), *meconidine* ($C_{21}H_{23}NO_4$), *lanthopine* ($C_{23}H_{25}NO_4$). A little acetic acid also exists in all opium (D. Brown).

Analytical Reactions.

First Analytical Reaction.—To a minute fragment of a salt of morphine add one drop of water, and warm the mixture until the salt dissolves, then stir the liquid with a glass rod moistened by a strong *neutral* solution of perchloride of iron; a dirty-blue color is produced. This effect is not observed in dilute solutions.

Second Analytical Reaction.—To a drop or two of a strong solution of a morphine salt in a test-tube add a minute fragment of iodic acid (HIO_3; page 293); iodide is set free. Into the upper part of the tube insert a glass rod covered with mucilage of starch, and warm the solution; dark-blue starch iodide is produced. If the mixture of morphine and iodic acid be shaken up with chloroform or bisulphide of carbon, a violet solution is obtained.

This reaction is only confirmatory of others, as albumenous matters also reduce iodic acid.

Third Analytical Reaction.—To a few drops of an aqueous infusion of opium add a drop of *neutral* solution of perchloride of iron; a red solution of meconate of iron is produced. Add solution of corrosive sublimate; the color is not destroyed (as it is in the case of sulphocyanate of iron, a salt of similar tint).

In cases of poisoning by a preparation of opium this test is almost as conclusive as a direct reaction of morphine (the poison itself), meconic acid being obtainable from opium only.

Other Reactions.—Add carbonate of sodium to a solution of a salt of morphine; a white precipitate of morphine falls, slowly and of a crystalline character if the solution is dilute. Collect this precipitate, and moisten it with neutral solution of perchloride of iron; the bluish tint above referred to is produced. ——Add an alkali to a solution of hydrochlorate or acetate of the alkaloid; morphine is precipitated, soluble in excess of the fixed alkali; far less readily so in ammonia.——Moisten a particle of a morphine salt with nitric acid; an orange-red coloration is produced.——To morphine add strong sulphuric acid, mix, and strew nitrate of bismuth on the fluid; the mixture turns dark brown or black.——Heat morphine on platinum foil; it burns entirely away.

Apomorphine ($C_{17}H_{17}NO_2$).

Apomorphine (*ἀπὸ*, *apo*, from, and *morphine*) is an alkaloid obtained from morphine by Matthiessen and Wright. It possesses remarkable physiological effects: one-tenth of a grain (in aqueous solution) injected under the skin, or one quarter of a grain taken into the stomach, is said to produce vomiting in from four to ten minutes.

Process.—Hydrochlorate of morphine is hermetically sealed in a thick tube with considerable excess of hydrochloric acid, and heated to nearly 300° F. for two or three hours. The product is purified by diluting the contents of the tube with water, precipitating with bicarbonate of sodium, and treating the precipitate with ether or chloroform. On shaking up the ethereal or chloroform solution with a very small quantity of strong hydrochloric acid, the sides of the vessel become covered with crystals of the hydrochlorate of the new base. These may be drained from the mother-liquor, washed with a little cold water, in which the salt is sparingly soluble, recrystallized from hot water, and dried on bibulous paper or over sulphuric acid. The formula ($C_{17}H_{17}NO_2,HCl$) indicates that the new alkaloid is derived from morphine by abstraction of the elements of water.

Hydrochlorate of apomorphine (*Apomorphinæ Hydrochloras*, U. S. P.) occurs in "colorless or grayish-white, shining crystals, turning greenish on exposure to light and air, odorless, having a bitter taste and a neutral or faintly acid reaction. Soluble in 6.8 parts of water and in 50 parts of alcohol at 15° C. (59° F.); slowly decomposed by boiling water or boiling alcohol; almost insoluble in ether or chloroform; should it impart color to either of these liquids it should be rejected, or it may be purified by thoroughly agitating it with either liquid, filtering, and then rapidly drying the salt on bibulous paper in a dark place. The aqueous solution, on gentle warming, rapidly turns green, but retains a neutral reaction. Solution of bicarbonate of sodium, added to an aqueous solution of the salt, throws down the white, amorphous alkaloid, which soon turns green on exposure to air, and forms a bluish-green solution with alcohol, a purple one with ether or pure benzol, and a violet or blue one with chloroform."

Codeine also, according to the same chemists, yields apomorphine by similar treatment, a reaction that would seem to indicate that codeine is methyl-morphine; indeed, Grimaux (Hesse also) has since obtained codeine—or, possibly, an isomer of codeine, methyl-morphine—from morphine.

$$\underset{\text{Codeine.}}{C_{17}H_{17}CH_3HNO_3} + HCl = \underset{\text{Chl. of methyl.}}{CH_3Cl} + H_2O + \underset{\text{Apomorphine.}}{C_{17}H_{17}NO_2}$$

Dr. C. R. A. Wright has recently obtained several new derivatives of codeine.

Codeine neither gives a blue color with ferric chloride nor a red with nitric acid. Both codeine and morphine, when heated with a mixture of strong sulphuric acid and arseniate of sodium, give a blue color, the morphine yielding a greenish-blue and the codeine a violet-blue.

QUESTIONS AND EXERCISES.

669. Write some general formulæ of artificial alkaloids.

670. Name the substances represented by the following formulæ:—

$$\left.\begin{array}{r}C_3H_7\\H\\H\end{array}\right\}N,\qquad\left.\begin{array}{r}C_3H_7\\C_3H_7\\H\end{array}\right\}N,\qquad\left.\begin{array}{r}CH_3\\C_2H_5\\C_5H_{11}\end{array}\right\}N.$$

$$\left.\begin{array}{r}CH_3\\H\\H\end{array}\right\}N,\qquad\left.\begin{array}{r}CH_3\\CH_3\\H\end{array}\right\}N,\qquad\left.\begin{array}{r}CH_3\\CH_3\\CH_3\end{array}\right\}N.$$

671. What is the assumed constitution of the salts of the alkaloids?

672. Describe the treatment in cases of poisoning by alkaloids.

673. Give the process for the preparation of Hydrochlorate of Morphine. In what form does morphine occur in opium?

674. How is Acetate of Morphine prepared?

675. What plan is adopted for preventing the decomposition of the official solutions of morphine?

676. Mention the analytical reactions of morphine.

677. In addition to the reactions of morphine, what test may be employed in searching for opium in a liquid or semi-fluid material?

678. How is Apomorphine prepared, and what are its properties?

679. Describe the relation of morphine to codeine.

QUININE, OR QUINIA.

Formula $C_{20}H_{24}N_2O_2,3H_2O$. Molecular weight 378.

Source.—Quinine (*Quinina*, U. S. P.) and other similar alkaloids exist in cinchona-bark as kinates. In the yellow bark (*Cinchona Flava*, U. S. P., from *Cinchona calisaya*) chiefly quinine is present; in the pale bark (*Cinchonæ Pallidæ Cortex*, B. P., chiefly from *C. officinalis*) other alkaloids are more frequently found; while in the red bark (*Cinchona Rubra*, U. S. P.) these alkaloids occur in irregular proportions.

Under *Cinchona* the United States Pharmacopœia recognizes "the bark of any species of *Cinchona* containing at least 3 per cent. of its peculiar alkaloids."

Extraction of the Mixed Alkaloids.—Take 750 grains of finely powdered bark. Make it into a paste with milk of lime (slaked lime about 400 grains and water about 4 ounces). Dry the mixture over a water-bath. Powder the residue and place the whole in a cylindrical percolator. Pour in 3½ fluidounces of chloroform. When, after standing, packing is complete, allow percolation to commence and to proceed slowly. After a time pour 3½ fluidounces more chloroform into the percolator. When percolation has ceased transfer the percolate to a retort, and add nearly half an ounce of water and enough dilute sulphuric acid to make the mixture acid to test-paper. Recover the chloroform by distilling from a water-bath, and allow the residue to cool; filter. To the filtrate, which contains the alkaloids as acid sulphates, add ammonia in slight excess. Collect the precipitated alkaloids on a filter, wash, and dry in the air or over a dish of sulphuric acid covered by a bell-jar. (For the separation of alkaloids see Index, " Dr. Vrij's process," an operation which should not be attempted at this stage of study.)

Process for Sulphate.—Sulphate of quinine (*Quininæ Sulphas*, U. S. P.) may be prepared by treating the yellow bark with dilute hydrochloric acid, precipitating the resulting solution of hydrochlorate of quinine by soda, and redissolving the precipitated quinine in the proper proportion of hot dilute sulphuric acid. This, the common commercial sulphate, crystallizes out on cooling in silky acicular crystals, one molecule containing two atoms of quinine ($2C_{20}H_{24}N_2O_2$), one of sulphuric acid (H_2SO_4), and seven of water of crystallization ($7H_2O$).

In the process of the former United States Pharmaeopœia (1870) lime was used instead of soda, the precipitated quinine dissolved in boiling alcohol, the latter recovered by distillation, the residual quinine neutralized by diluted sulphuric acid, the solution treated with animal charcoal, filtered while hot, set aside to crystallize, and recrystallized if necessary.

Sulphate of quinine, the *common* or so-called *disulphate* $(C_{20}H_{24}N_2O_2)_2,H_2SO_4,8H_2O$, is only slightly soluble in water; on the addition of dilute sulphuric acid the so-called *neutral sulphate*, or *soluble sulphate* (*Quininæ Bisulphas*, U. S. P.; $C_{20}H_{24}N_2O_2,H_2SO_4,7H_2O$), is formed, which is freely soluble. The latter salt may be obtained in large rectangular prisms.* An *acid sulphate* ($C_{20}H_{24}N_2O_2,2H_2SO_4,7H_2O$) also exists.

The ordinary disulphate of quinine is more soluble in alcohol or alcoholic liquids than in water. The citrate of iron and quinine (*Ferri et Quininæ Citras*, U. S. P.) is the well-known scale compound. It is made by dissolving ferric hydrate, prepared from ferric sulphate, and quinine, prepared from the sulphate, in solution of citric acid; the liquid, evaporated to a syrupy consistence and dried in thin layers on glass plates, yields the usual greenish-yellow scales (*vide* p. 151).

Quininæ Valerianas, U. S. P., may be made by dissolving precipitated quinine in warm aqueous solution of valerianic acid and setting aside to crystallize. Its formula is $C_{20}H_{24}N_2O_2,C_5H_{10}O_2,H_2O$.

Basic Citrate of Quinine has the formula $(C_{20}H_{24}N_2O_2)_2,H_3C_6H_5O_7,$-

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* We do not know whether or not these sulphates are ordinary sulphates, the hydrogen of the acid going over to the quinine molecule, nor whether or not the quinine molecule is univalent or bivalent; hence we cannot say whether the *common* sulphate or the *soluble* sulphate is, in constitution, the neutral sulphate. In the above paragraph the names *disulphate, neutral sulphate, acid sulphate*, indicate nothing more than that the first sulphate contains in one molecule two atoms (chemical atoms) of quinine to one of sulphuric acid, the second one of each, and the third two of acid to one of quinine.

$5H_2O$. Other citrates contain three molecules of quinine to two of citric acid, and one of quinine to one of citric acid.

Quininæ Hydrobromas, U. S. P., has the formula $C_{20}H_{24}N_2O_2,HBr,$-$2H_2O$.

Quininæ Hydrochloras, U. S. P., has the formula $C_{20}H_{24}N_2O_2,HCl,$-$2H_2O$.

REACTIONS.

First Analytical Reaction.—To a solution of quinine or its salts in acidulated water add fresh chlorine-water, shake, and then add solution of ammonia; a green coloration (thalleiochin, or dalleiochin) is produced. Bromine-water or bromine-vapor may be used instead of chlorine.

Second Analytical Reaction.—Repeat the foregoing reaction, but precede the addition of solution of ammonia by that of solution of ferrocyanide of potassium; an evanescent red coloration is produced (Livonius and Vogel).

Third Analytical Reaction.—To an aqueous solution of a soluble salt of quinine add solution of oxalate of ammonium; a white crystalline precipitate of oxalate of quinine falls. It is soluble in acids. If the solution to be tested be made from ordinary sulphate of quinine, excess of the latter should be added to water very faintly acidulated with sulphuric acid, and the undissolved crystals removed by filtration.

Fourth Analytical Reaction.—A saturated aqueous solution of any neutral salt of quinine is made by dissolving so much of the salt in hot water as that some shall separate when the mixture has cooled to about 60° F. After standing for some time, filter. To one volume of the filtrate one-half volume of water-washed ether is added, and then ammonia in slight excess. After agitation and rest for fifteen minutes all alkaloid precipitated by the ammonia will have dissolved.

Note.—In the case of quinidine salts well-defined crystals will appear at the junction of the aqueous and ethereal layers, especially after standing. In the case of cinchonidine salts a thick layer of small crystals makes its appearance at once, whilst in the case of cinchonine salts the undissolved alkaloid is enough to make the ethereal layer nearly solid.

Fifth Analytical Reaction.—Formation of Iodo-sulphate of Quinine. Dissolve sulphate of quinine in weak spirit of wine slightly acidulated with sulphuric acid, and add an alcoholic solution of iodine; a black precipitate forms. Allow the precipitate to settle, pour away the fluid, wash once or twice with alcohol, and then boil with alcohol; on cooling, minute crystals separate having the optical properties of the mineral tourmaline. This iodo-sulphate is sometimes termed Herapathite, from the name of its discoverer. It is so slightly soluble in alcohol that by its means quinine can be separated from its admixture with the other cinchona alkaloids. According to Jörgensen, it has the formula $4C_{20}H_{24}N_2O_2,3H_2SO_4,2HI,I_4,xH_2O$.

Sixth Analytical Reaction.—Prepare a saturated solution of ordinary sulphate of quinine in water at about 60° F., and add to 5 volumes of that solution 7 volumes of solution of ammonia (sp. gr. 0.96). The alkaloid which at first precipitates redissolves upon slight agitation if the sulphate of quinine is free from anything but traces of other cinchona alkaloids. If, however, more than traces of quinidine, cinchonidine, and cinchonine salts be present a permanent precipitate remains. This is Kerner's method of testing sulphate of quinine for other cinchona alkaloids. It turns upon the fact that the solubility of the sulphates of the cinchona alkaloids in water is in the opposite order to the solubility of the alkaloids themselves in solution of ammonia.

Other Characters.—Concentrated sulphuric acid dissolves quinine with production of only a faint yellow color, which distinguishes it from salicin.——Quinine and its salts, heated on platinum foil, burn entirely away.——Most salts of quinine when in solution have a beautiful blue fluorescence. They twist the ray of polarized light to the left. Quinine is soluble in alcohol, ether, benzol, and chloroform. Ordinary quinine sulphate is insoluble in chloroform, and but slightly soluble in water. Its solubility in chloroform is increased by the presence in solution of quinidine and cinchonine sulphates (Prescott), and its solubility in water is decreased by the presence in solution of ammonium sulphate (Carles). The slight solubility of its sulphate and iodo-sulphate in water distinguishes quinine from the other cinchona alkaloids, including the "amorphous alkaloid," or "quinoidine."

Quinidine or *Quinidia* ($C_{20}H_{24}N_2O_2$, the Conquinine or Conchinine of Hesse) is an isomer of quinine. Its salts are fluorescent, and give thalleioquin with chlorine- or bromine-water and ammonia. They twist the ray of polarized light to the right. Quinidine is insoluble in water and sparingly soluble in ether (see Quinine, 4th Analytical Reaction). It is soluble in alcohol, benzol, and chloroform. It is less soluble than quinine in ammonia, 5 volumes of a saturated aqueous solution of its ordinary sulphate requiring 60 to 80 volumes of ammonia solution (sp. gr. 0.96). Its sulphate (*Quinidinæ Sulphas*, U. S. P.; $2C_{20}H_{24}N_2O_2,H_2SO_4,2H_2O$) is more soluble in water and chloroform than the sulphate of quinine. Tartrate of quinidine is soluble in water. The hydriodate is insoluble in water and weak spirit, and occurs as sandy crystals. The hydriodates of the other cinchona alkaloids, though more soluble than quinidine hydriodate, are sometimes precipitated from neutral concentrated solutions as amorphous or semi-liquid precipitates. These, however, are soluble in weak spirit. "If 0.5 gm. each of sulphate of quinidine and of iodide of potassium (not alkaline to test-paper) be agitated with 10 c.c. of water at about 60° C. (140° F.), the mixture then macerated at 15° C. (59° F.) for half an hour, with frequent stirring, and filtered, the addition to the filtrate of a drop or two of water of ammonia should not cause more than a slight turbidity (abs. of more than small proportions of cinchonine, cinchonidine, or quinine)."—U. S. P.

Cinchonidine or *Cinchonidia* ($C_{20}H_{24}N_2O$).—When perfectly pure, salts of cinchonidine do not give thalleioquin and are not fluorescent. Even good commercial salts, however, nearly always give both reactions. Salts of cinchonidine twist the polarized ray to the left. Cinchonidine is insoluble in water and nearly so in ether (see Quinine, 4th Analytical Reaction). It is soluble in alcohol, benzol, and chloroform. It is less soluble in ammonia solution than quinine, five volumes of a saturated aqueous solution of cinchonidine sulphate requiring about 80 volumes of ammonia solution (sp. gr. 0.96). It is true that cinchonidine is dissolved as readily as quinine if excess of strong ammonia is quickly mixed with the solution of a salt of cinchonidine; but from such a solution cinchonidine soon crystallizes, while quinine remains dissolved for many hours. Sulphate (*Cinchonidinæ Sulphas*, U. S. P. $(C_{20}H_{24}N_2O)_2,H_2SO_4,3H_2O$) and hydriodate of cinchonidine are soluble in water, but the sulphate, like quinine sulphate, is insoluble in chloroform. Tartrate of cinchonidine is insoluble in water, and in this form cinchonidine is usually separated from neutral solutions containing the other cinchona alkaloids except quinine.

Cinchonine or *Cinchonia* ($C_{20}H_{24}N_2O$) (*Cinchonina*, U. S. P.) is an isomer of cinchonidine. When quite pure its salts are not fluorescent and do not give thalleioquin. As in the case of cinchonidine, even good commercial specimens of cinchonia salts nearly always give both reactions. Cinchonia salts twist the polarized ray to the right. Cinchonine is insoluble in water and nearly so in ether (see Quinine, 4th Analytical Reaction). It is soluble in chloroform, benzol, and alcohol. Chloroform containing one-fourth of its weight of 95-per cent. alcohol dissolves cinchonine much more readily than either alcohol or chloroform alone. Cinchonine is insoluble in ammonia solution. Sulphate (*Cinchoninæ Sulphas*, U. S. P.) $(C_{20}H_{24}N_2O)_2,H_2SO_4,2H_2O$, tartrate, and hydriodate of cinchonine, are soluble in water, and the sulphate, like sulphate of quinidine, is soluble in chloroform. In mixtures of cinchona alkaloids this alkaloid is precipitated by alkali after the others have been successively removed by ether, tartrate of sodium, and iodide of potassium.

Cinchonine heated with strong potash or soda yields an oily alkaloid termed *chinoline* (C_9H_7N), a body which exists in coal-tar, and which may be obtained artificially (Skraup) by the action of caustic potash on a mixture of nitrobenzine and aniline in the presence of glycerin. It forms crystalline salts with acids.

"*Quinoidine*" or "*Quinoidia,*" or the "*Amorphous Alkaloid*" (*Chinoidin,* U. S. P.).—Cinchona-barks generally contain some alkaloid isomeric with quinine, which, like quinine, is soluble in ether, but the ordinary sulphate and iodo-sulphate of which are not crystalline and are soluble. These salts are semi-solid, resinous-looking substances. The iodo-sulphate is used in Dr. Vrij's method for the separation of mixed alkaloids (see Index). Quinoidine is usually obtained along with quinine, etc. from the mixed alkaloids by ether, and remains in the mother-liquor, from which it is precipitated by an alkali. If quinoidine be triturated with boiling water, the liquid, after filtration, should be clear and colorless, and should remain so on the addition of an alkali (abs. of alkaloidal salts). On ignition, quinoidine should not leave more than 0.7 per cent. of ash.

Cinchovatine or *Cinchovatia* occurs in a particular variety of cinchona-bark. *Quinicine* or *Quinicia* and *Cinchonicine* or *Cinchonicia* are alkaloids produced by the action of heat on quinine or quinidine and on cinchonine or cinchonidine respectively. They also are isomers—Hesse says polymers—of the parent alkaloids. Both yield ordinary salts. *Quiniretin* is the name given to the brown or reddish-brown indifferent substance into which quinine in aqueous solution is converted when exposed to much light.

Quinamine or *Quinamia* ($C_{20}H_{26}N_2O_2$) is a fifth cinchona alkaloid obtained by Hesse in 1872 from the bark of *Cinchona succirubra.* Its solution is not fluorescent and does not give thalleioquin. The same chemist announces the presence in cinchona of a sixth alkaloid, *cinchamidine* ($C_{20}H_{26}N_2O$).

Cupreine, homoquinine, or *ultraquinine* are names given to an alkaloid existing in the bark of a Remijia (allied to Cinchona), and termed *cuprea*-bark. It closely resembles quinine, but it is sparingly soluble in ether.

STRYCHNINE, OR STRYCHNIA.

Formula $C_{21}H_{22}N_2O_2$. Molecular weight 334.

Source.—This alkaloid (*Strychnina,* U. S. P.) exists, to the extent of 0.2 to 0.5 per cent., in the seed of *Strychnos Nux Vomica* (*Nux Vomica,* U. S. P.), also (Shenstone) in minute quantity in the bark of the Nux Vomica tree (false Angostura-bark), and to 1.0 or 1.5 per cent. in St. Ignatius's bean (*Strychnos Ignatia*) (*Ignatia,* U. S. P.), chiefly in combination with strychnic or igasuric acid, or, after slight fermentation when moistened, with lactic acid.

Process.—According to the British official process for its preparation, the nuts, disintegrated by subjection to steam, and, after drying, grinding in a coffee-mill, are exhausted with spirit, the latter removed by distillation, the extract dissolved in water, coloring and acid matters precipitated by acetate of lead, the filtered liquid evaporated to a small bulk, the strychnine precipitated by ammonia, the precipitate washed, dried, and exhausted with spirit, the spirit recovered by distillation, and the residual liquid set aside to crystallize. Crystals of strychnine having formed, the mother-liquor (which contains the brucine of the seeds) is poured away, and the crystals of strychnine washed with spirit (to remove any brucine) and recrystallized.

In the U. S. P. (1870) process the rasped Nux Vomica is exhausted by very dilute hydrochloric acid, milk of lime added to the evaporated decoction to decompose the hydrochlorate of strychnine, the precipitated and dried mixture of strychnine and lime treated with diluted alcohol to remove brucine, and then with strong, hot alcohol to dissolve out strychnine; the alcohol having been recovered by distillation, the residual impure strychnine is dissolved in very dilute sulphuric acid, the solution decolorized by animal charcoal, evaporated, and set aside to crystallize, the crystals of sulphate of strychnine (*Strychninæ Sulphas*, U. S. P.; $2C_{21}H_{22}N_2O_2,H_2SO_4,7H_2O$; Coleman, $6H_2O$) redissolved in water, ammonia added to precipitate pure strychnine, and the latter dried. It is soluble in about 40 parts of water.

Properties.—Strychnine occurs "in right square octahedrons or prisms, colorless and inodorous; sparingly soluble in water, but communicating to it its intensely bitter taste; soluble in boiling rectified spirit and in chloroform, but not in absolute alcohol or in ether."

REACTIONS.

First Analytical Reaction.—Place a minute particle of strychnine on a white plate, and near to it a small fragment of red chromate of potassium; to each add one drop of concentrated sulphuric acid; after waiting a minute or so for the chromate to fairly tinge the acid, draw the latter, by a glass rod, over the strychnine spot; a beautiful purple color is produced, quickly fading into a yellowish-red. The following oxidizing agents may be used in the place of the chromate: puce-colored oxide of lead, fragments of black oxide of manganese, ferridcyanide of potassium, or permanganate of potassium.

This reaction is highly characteristic: a minute fragment dissolved in much dilute alcohol—or, better, chloroform—and one drop of the liquid evaporated to dryness on a porcelain crucible-lid or other white surface, yields a residue which immediately gives the purple color on being oxidized in the manner directed.

Other Reactions.—Strong sulphuric acid does not decompose strychnine even at the temperature of boiling water, a fact of which advantage is taken in separating strychnine from other organic matter for purposes of toxicological analysis.——Sulphocyanide of potassium produces, even in dilute solutions of strychnine, a white precipitate, which under the microscope is seen to consist of tufts of acicular crystals.——Strong nitric acid does not color strychnine in the cold, and on heating only turns it yellow.

The Physiological Test.—A small frog placed in an ounce of water to which $\frac{1}{100}$ of a grain of a salt (acetate) of strychnine is added is in two or three hours seized with tetanic spasms on the slightest touch, and dies shortly afterward.

Strychnine has an intensely bitter taste. Cold water dissolves only $\frac{1}{2000}$ part, yet this solution, even when largely diluted, is distinctly bitter. Alcohol is a somewhat better solvent. The salts of the alkaloid are more soluble. The *Liquor Strychniæ*, B. P., contains four grains of strychnine to the ounce, the solvent being three parts water. one part spirit, and a few minims (6 per ounce) of hydrochloric acid (rather more than sufficient to form hydrochlorate of strychnine). A syrup of Phosphates of Iron, Quinine, and Strychnine is official (*Syrupus Ferri, Quininæ, et Strychninæ Phosphatum*). It contains 1 part of strychnine in 2500.

Brucine, or Brucia ($C_{23}H_{26}N_2O_4,4H_2O$), is an alkaloid accompanying strychnine in Nux Vomica and St. Ignatius's bean to the extent of about 0.5 per cent. It is readily distinguished by the intense red color produced when nitric acid is added to it. *Igasurine*, once supposed to be a third alkaloid of nux vomica, has been shown by Shenstone to be only a mixture of brucine and strychnine.

Curarine ($C_{10}H_{15}N$), the active principle of the arrow-poison termed *urari*, *ourari*, *wourali*, or *woorara*, prepared from a *Strychnos*, resembles strychnine in giving color by oxidation, but the color is more stable. Iodide or platino-cyanide of potassium does not with curarine afford precipitates which crystallize from alcohol like those of strychnine. Curarine also is soluble in water. Unlike strychnine, curarine is reddened by sulphuric acid; it, also, is not dissolved out by ether from an acid or alkaline liquid. *Curari* appears to vary much in strength and quality. It is probably a mixture of vegetable extracts.

Distinction of Brucine from Morphine.—The red coloration produced by the action of nitric acid on brucine is distinguished from that yielded by morphine by the action of reducing agents (such as stannous chloride, hyposulphite of sodium, sulphydrate of sodium), which decolorize the morphine red, but change that of the brucine to violet and green (Cotton).

Distinction of Free Alkaloids or their Salts from Each Other.—This is accomplished by remembering the appearance and other physical characters of the substances as met with in pharmacy, the effect of heat, the action of such solvents as water, alcohol, and ether, the influence of strong and diluted acids, strong and weak alkalies, oxidizing agents, chlorine-water and ammonia, and other reagents. (See annexed Tables, I. and II.)

QUESTIONS AND EXERCISES.

680. What alkaloids are more or less characteristic of the different varieties of cinchona-bark? In what form do they occur?

681. By what method is Disulphate of Quinine obtained?

682. Give the characters of disulphate of quinine.

683. Describe the tests for quinine.

To face page 391.]

I. TABLE FOR THE IDENTIFICATION OF THE FOLLOWING ALKALOIDS, ACIDS, ETC.

(*Compiled by* A. SENIER, M. D.)

MORPHINE. BRUCINE.		SALICIN. STRYCHNINE.		QUININE. QUINIDINE.	CINCHONINE. CINCHONIDINE.		ACIDS. { SULPHURIC. HYDROCHLORIC. PHOSPHORIC.			ACETIC. MECONIC. CITRIC.	
To a small quantity on a white plate add strong nitric acid.		If no Morphine or Brucine, moisten a small quantity on a white plate with strong sulphuric acid.		If Morphine, Brucine, Salicin, and Strychnine are absent, make a saturated solution in hot water and cool down to about 60° F., removing the crystals which have deposited by filtration. If the substance is an alkaloid or an acid salt, it must be neutralized. To one volume of this solution in a test-tube add exactly half a volume of ether and then ammonia solution in slight excess. Agitate and set aside for a quarter of an hour.			Make a solution with a slight excess of nitric acid, divide it into three portions, and test as follows:—			Make a neutral solution, divide it into two portions, and test as follows:—	
An Orange Color, decolorized by $SnCl_2$, $Na_2S_2O_3$, or $NaHS$ =*Morphine.** Confirm by—Fe_2Cl_6(neut.), which gives with morphine or its salts a blue color. HIO_3 is decomposed by morphine or its compounds, with liberation of iodine, which may be recognized by starch.	*A Red Color.* To a few grains in a test-tube add a drop or two of HNO_3: warm to boiling and dilute with water; then add a few drops of stannous chloride. A violet color = *Brucine.*	*A deep red color = Salicin.* Confirm by boiling the substance with water to which has been added a few drops of dilute H_2SO_4. Then make solution alkaline and examine for glucose.	*No color, or only a slight color.* Draw a moistened crystal of $K_2Cr_2O_7$ across the acid film when a transient play of colors, violet to red = *Strychnine.*	*Precipitate entirely soluble in the ether.* To a portion of the saturated aqueous solution add rather more than an equal bulk of ammonia solution (sp. gr. 0.96) and agitate. The precipitate dissolves completely = *Ordinary Sulphate of Quinine.* If precipitate does not dissolve completely, add to another portion of the aqueous solution $(NH_4)_2C_2O_4$ and agitate (no precipitate at once with ordinary sulphate of quinine). A bulky crystalline precipitate = *Quinine.* Confirm by other reactions (see Quinine).	*A crystalline layer between the ethereal and aqueous solutions.* To a portion of the aqueous solution add $Na_2C_4H_4O_6$ and agitate. A bulky crystalline precipitate = *Cinchonidine.* Confirm by other reactions (see Cinchonidine). If no precipitate or only a trace, add to another portion of the aqueous solution KI. A heavy white precipitate = *Quinidine.* If the precipitate be semi-liquid, it contains cinchonidine or other alkaloids, the hydriodates of which are soluble in weak spirit.	*Precipitate insoluble in ether = Cinchonine.* Confirm by other reactions (see Cinchonine).	*First portion.* Add $BaCl_2$. A precipitate = *Sulphuric Acid.*	*Second portion.* Add $AgNO_3$. A precipitate = *Hydrochloric Acid.*	*Third portion.* Boil for a time and then add a few drops of an excess of solution of molybdate of ammonium in HNO_3, and boil. A yellow pulverulent precipitate = *Phosphoric Acid.*	*First portion.* Add neutral Fe_2Cl_6. A red color indicates acetic or meconic acid. Distinguish. Decolorized by boiling=*Acetic Acid.* Not decolorized by boiling = *Meconic Acid.*	*Second portion.* If no acetic or meconic acid, add $AgNO_3$. Precipitate (white, with a tendency to darken) soluble in HNO_3 =*Citric Acid.* Confirm by adding $CaCl_2$ to a neutral conc. solution and boiling, when a white precipitate of citrate of calcium separates.

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* Strychnine of commerce often gives an orange or red color, due to contamination with brucine.

To face page 391.]

II. TABLE FOR THE QUALITATIVE ANALYSIS OF ORDINARY SCALE COMPOUNDS.

(*Compiled by* A. SENIER, M. D.)

<table>
<tr>
<td colspan="4">ALKALOIDS. { QUININE.
QUINIDINE.
BEBERINE.
CINCHONINE.
CINCHONIDINE.
STRYCHNINE.</td>
<td colspan="4">ACIDS. { PYROPHOSPHORIC.
HYPOPHOSPHOROUS (generally converted into pyrophosphoric).
SULPHURIC.
HYDROCHLORIC (as a contamination).
TARTARIC.
CITRIC.</td>
<td>INORGANIC BASES. { AMMONIUM (often as a contamination).
FERRIC IRON.
POTASSIUM.
SODIUM.</td>
</tr>
<tr>
<td colspan="4">Dissolve a portion in H_2O, and add NH_4HO cautiously (Precipitate = Alkaloids (except Strychnine) and sometimes Fe_26HO). Agitate the mixture with a little ether, and separate, by means of a pipette, the ethereal solution, aqueous solution, and insoluble precipitate.</td>
<td colspan="4">Ignite a small quantity of the scale. Heat the ash with HNO_3, and add to an excess of solution of ammonium molybdate in HNO_3, and boil.</td>
<td rowspan="5"><i>Ammonium.</i>—Boil aqueous solution of scale with KHO and test vapor for NH_3. Filter and dissolve precipitate in HCl, and test the solution for <i>Iron</i> by K_4FeCy_6, KCyS, etc.
<i>Potassium and Sodium.</i>—Ignite a small quantity of the scale, and moisten the residue with water. Test moistened residue with litmus-paper. If alkaline, examine for potassium and sodium by the color imparted to flame, and for potassium by HCl and $PtCl_4$.</td>
</tr>
<tr>
<td colspan="2">ETHEREAL SOLUTION.</td>
<td>INSOLUBLE PRECIPITATE.</td>
<td>AQUEOUS SOLUTION.</td>
<td colspan="2">A YELLOW PRECIPITATE.</td>
<td colspan="2">NO YELLOW PRECIPITATE.</td>
</tr>
<tr>
<td colspan="2">May contain quinine, quinidine, or beberine. To solution in a test-tube add H_2O, very slightly acidulated with $HC_2H_3O_2$ and boil, burning off the ether. To a portion of the acetic solution add Cl or Br water and afterward NH_4HO.</td>
<td rowspan="4">Is cinchonine, cinchonidine, or Fe_26HO.
Saturate a drop or two of acetic acid in a little water with the precipitate, and to part of the solution add $Na_2C_4H_4O_6$, when a precipitate occurs in the case of <i>cinchonidine</i>, and no precipitate in that of <i>cinchonine</i>.</td>
<td rowspan="4">May contain strychnine. Agitate with $CHCl_3$ and separate chloroformic solution. Evaporate chloroformic solution, and moisten residue with concentrated H_2SO_4. Draw across the acid film a small moistened crystal of $K_2Cr_2O_7$ when a transient play of colors—violet to red = <i>strychnine</i>. No colors = no strychnine. In case of doubt add NH_4HO to original solution. Agitate with chloroform, and proceed as before.</td>
<td colspan="2">Pyrophosphoric or hypophosphorous acid. Precipitate some of the aqueous solution with KHO, filter, neutralize with HNO_3 and add $AgNO_3$.</td>
<td colspan="2">Precipitate some of the aqueous solution with KHO, filter, and add to a portion of the filtrate a slight excess of HNO_3 and divide into two parts. To one add $BaCl_2$ (precipitate = <i>Sulphuric Acid</i>). To the other add $AgNO_3$ (precipitate = <i>Hydrochloric Acid</i>). Neutralize another portion of the KHO filtrate with HNO_3 and add $AgNO_3$.</td>
</tr>
<tr>
<td>GREEN COLOR (thalleioquin).</td>
<td>NO GREEN COLOR.</td>
<td rowspan="3">White precipitate soluble in nitric acid = <i>Pyrophosphoric Acid.</i></td>
<td rowspan="3">White to black precipitate, soluble in nitric acid = <i>Hypophosphorous Acid.</i></td>
<td>PRECIPITATE GRAY TO BLACK.</td>
<td>PRECIPITATE WHITE.</td>
</tr>
<tr>
<td rowspan="2">Solution is fluorescent, and contains either quinine or quinidine. Concentrate the remainder of the solution and divide into two parts. To one add KI, and to the other add $(NH_4)_2C_2O_4$.
KI precipitates <i>quinidine</i>, not quinine.
$(NH_4)_2C_2O_4$ precipitates <i>quinine</i>, not quinidine.
For another method, see the third division of the annexed Table (I.) for alkaloids, using 40 or 50 grains of material.</td>
<td rowspan="2">To a portion of the acetic solution add KHO, a yellowish-white precipitate = <i>Beberine.</i></td>
<td>Add very little NH_4HO (not sufficient to dissolve the whole precipitate) and heat. A silver mirror = <i>Tartaric Acid.</i>
$CaCl_2$ and $Ca2HO$ precipitate neutral solution (if concentrated) in the cold, the precipitate redissolving on boiling.</td>
<td><i>Citric acid</i> gives no mirror. $CaCl_2$ and $Ca2HO$ do not precipitate citric acid in the cold, but upon boiling (if solution be sufficiently concentrated) precipitation occurs.</td>
</tr>
<tr>
<td colspan="3"><i>Confirm Tartaric or Citric Acid.</i>—To slightly acidified KHO filtrate add NH_4HO in slight excess and considerable quantity of NH_4Cl and $CaCl_2$. <i>Tartrates</i> are precipitated completely in the cold with agitation and rest for about ten minutes. To the solution (or filtrate if tartrates are present) add three volumes of spirit of wine, when <i>Citrates</i> are precipitated. If sulphates have been found, disregard slight precipitate with spirit of wine.</td>
</tr>
</table>

684. How is the adulteration of disulphate of quinine by salicin detected?

685. Show how the sulphates of quinine or cinchonine may be proved to be present in commercial quinine.

686. How are cinchonine and quinine distinguished from morphine?

687. Whence is strychnine obtained?

688. Describe the official process for the isolation of strychnine.

689. Give the characters of strychnine.

690. Enumerate the tests for strychnine, and describe their mode of application.

691. By what reagent is brucine distinguished from strychnine?

692. Distinguish between brucine and morphine.

693. By what general methods would you distinguish common alkaloids from each other?

Analytical Exercises.—Analyze small quantities of alkaloids, their salts, and various "scale" compounds by aid of the annexed Tables, I. and II.

ALKALOIDS OF LESS FREQUENT OCCURRENCE.

Aconitine, Aconitina, or Aconitia is an alkaloid obtained from aconite (*Aconitum Napellus*) leaves (*Aconiti Folia*, B. P.) and root (*Aconitum*, U. S. P.). The alkaloid itself is only slightly soluble in water; it occurs in the plant in combination with a vegetable acid, forming a soluble salt.

Process.—The process for the preparation of *Aconitine*, B. P., consists in dissolving out the natural salt of the alkaloid from the root by rectified spirit, recovering the latter by distillation, mixing the residue with water, filtering, precipitating the aconitine by ammonia, drying the precipitate and digesting it in ether (in which some of the accompanying impurities are insoluble), recovering the ether by distillation, dissolving the dry residue in the retort in water acidulated by sulphuric acid, again precipitating the alkaloid by ammonia, and finally washing and drying.

Properties.—Aconitine usually occurs as a white powder, but has been obtained and studied in the crystalline state by Groves, Wright, and others. It is soluble in 150 parts of cold water, 50 of hot, and is much more soluble in alcohol and ether. It is one of the most violent poisons known. "When rubbed on the skin it causes a tingling sensation, followed by prolonged numbness."

The thousandth part of a grain on the tip of the tongue produces, after a minute or so, a characteristic tingling sensation and numbness: larger quantities rubbed into the skin cause numbness and loss of feeling. Oil of vitriol turns it of a yellowish, and afterward dirty-violet, color.

According to Wright, who, in conjunction with Groves and Williams, worked by aid of grants from the British Pharmaceutical Conference, *Aconitum napellus* yields crystalline *aconitine*, $C_{33}H_{43}NO_{12}$, crystalline *pseud-aconitine*, $C_{36}H_{49}NO_{12}$, and a non-crystalline alkaloid.

The tuberous roots of *Aconitum ferox* and other species constitute the *bish* or *bikh* of India (*Aconiti ferocis Radix*, P. I.). It chiefly contains the variety of aconitine termed *pseud-aconitine*. Some of the aconitine of pharmacy is pseud-aconitine. According to Paul and Kingzett, the alkaloid of Japanese aconite has the formula $C_{29}H_{43}NO_9$, while Wright and Menke state that the formula is $C_{66}H_{88}N_2O_2$, and name it *japaconitine*.

Aconitum heterophyllum, *Atis*, or *Atees* (*Aconiti heterophylli Radix*, P. I.), contains no aconitine, but an alkaloid having the formula $C_{46}H_{74}N_2O_5$ (Broughton, in *Pharmacographia*).

ASPIDOSPERMINE is an alkaloid of *Quebracho blanco* bark (Fraude). Another and different alkaloid is *quebrachine* ($C_{21}H_{26}N_2O_3$) (Hesse). The latter chemist has isolated four other closely-related alkaloids, and two from *Quebracho colorado* bark.

ATROPINE, or ATROPIA ($C_{17}H_{23}NO_3$), exists in the Belladonna, or Deadly Nightshade (*Atropa belladonna; Belladonnæ Folia et Radix*, U. S. P.), as soluble acid malate of atropine.

Process.—It is obtained in the pure state by exhausting the root with spirit, precipitating the acid and some coloring-matter by lime, filtering, adding sulphuric acid to form sulphate of atropine (which is somewhat less liable to decomposition during subsequent operations than the alkaloid itself), recovering most of the spirit by distillation, adding water to the residue, and evaporating till the remaining spirit is removed; solution of carbonate of potassium is then poured in till the liquid is nearly but not quite neutral, by which resinous matter is precipitated; the latter is filtered away, excess of carbonate of potassium then added, and the liberated atropine dissolved out by shaking the liquid with chloroform. The latter solution, having subsided, is removed, the chloroform recovered by distillation, the residual atropine dissolved in warm spirit, coloring-matter separated by digesting the liquid with animal charcoal, the solution filtered, evaporated, and set aside to deposit crystals.

Solubility.—Atropine is sparingly soluble in water, the liquid giving an alkaline reaction—more soluble in alcohol and ether.

Tests.—Atropine solutions give with perchloride of gold a yellow precipitate. One drop of a dilute aqueous solution (two grains to the ounce) powerfully dilates the pupil of the eye. It is generally applied on a piece of thin tissue-paper or small disk placed between the eyelid and the eye. Baryta-water decomposes it into *tropine* ($C_8H_{15}NO$) and *tropic acid* ($C_9H_{10}O_3$), a molecule of water being absorbed; hence the atropine so called would seem to be *tropate of atropine*. Indeed, Ladenburg by combining tropic acid and tropine has produced a base indistinguishable from atropine. The same chemist by removing the elements of water from tropine gets *tropidine*, $C_8H_{13}N$. This is, possibly, an intermediate member of a group of monamines of which others are *conine*, $C_8H_{15}N$, and *collidine*, $C_8H_{11}N$, the latter a product of the destructive distillation of bone-oil, coal, quinine, etc.

Commercial atropine is said by Regnauld and Valmont to be a mixture of true atropine with hyoscyamine.

Preparations.—The alkaloid itself (*Atropina*) and its sulphate (*Atropinæ Sulphas.* $(C_{17}H_{23}NO_3)_2H_2SO_4$, a colorless powder soluble in water, made by neutralizing atropine with sulphuric acid) are official in the United States Pharmacopœia.

Beberine, Bebirine, Beberia, or Bibirina ($C_{18}H_{21}NO_3$), an alkaloid existing in the bark of Bebeeru or Bebiæ (*Nectandra Rodiæi*).

Process.—According to the British Pharmacopœia, it, or rather its sulphate, $C_{36}H_{42}N_2O_6,H_2SO_4$ (*Beberiæ Sulphas*, B. P.), may be prepared by exhausting the bark (*Nectandræ Cortex*, B. P.) with water acidulated by sulphuric acid, concentrating, removing most of the acid by lime, filtering, precipitating the alkaloid by ammonia, filtering, drying, dissolving in spirit (in which some accompanying matters are insoluble), recovering most of the spirit by distillation, neutralizing by dilute sulphuric acid, evaporating to dryness, dissolving the residual sulphate in water, evaporating to the consistence of a syrup, and spreading on glass plates, drying the product at 140° F. Thus obtained, it occurs in thin dark-brown translucent scales, yellow when powdered, strongly bitter, soluble in water and in alcohol. It is probably not a single definite salt.

Tests.—Alkalies give a pale-yellow precipitate of beberine when added to an aqueous solution of a salt of the alkaloid; the precipitate is soluble in ether. With red chromate of potassium and sulphuric acid beberine gives a black resin, and with nitric acid a yellow resin.

Buxine, from the bark of *Buxus sempervirens; Pelosine*, or *Cissampeline*, from the root (*Pareira*, U. S. P.) of *Chondodendron tomentosum;* and *Paricine*, from a false Para cinchona-bark, are probably identical with Beberine (Flückiger).

Nectandrine ($C_{20}H_{23}NO_4$).—Drs. Maclagan and Gamgee a few years ago discovered this second alkaloid in Bebeeru-bark. It differs from beberine in fusing when placed in boiling water, in being much less soluble in ether, in giving with strong sulphuric acid and black oxide of manganese a beautiful green and then violet coloration, and in having a distinct molecular weight. They gave the opinion that two other alkaloids exist in Bebeeru-bark.

Berberine, or Berberia ($C_{20}H_{17}NO_4$) is an alkaloid existing in several plants of the natural order *Berberideæ* (three species yield *Indian Barberry*, *Berberis Cortex*, P. I.), in Calumba-root (*Calumba*, U. S. P.), *Goldthread* (*Coptis trifolia*) according to Mayer in the root of *Coptis Sula*, or *Nieshnie Bitters* (*Captidis Radix*, P. I.), an Indian tonic, and in many yellow woods. *Hydrastis canadensis*, *Yellow-root* or *Golden Seal* (*Hydrastis*, U. S. P.), contains berberine, though another alkaloid, *hydrastine*, and even a third, are said to be present. *Xanthorrhiza apiifolia*, an old American tonic, and, apparently, *Xanthoxylum fraxineum*, or Prickly Ash bark (*Xanthoxylum*, U. S. P.), also contain berberine. The rhizome of *Menispermum canadense*, *Yellow Parilla* or *Canadian Moonseed* (*Menispermum*, U. S. P.), contains, according to Maisch, a colorless alkaloid as well as berberine. The color of the tissues of these vegetables is apparently due to berberine, for the alkaloid itself is remarkable for its beautiful yellow color.

Tests.—When a dilute solution of iodine in iodide of potassium is added to a solution of any salt of berberine in hot spirit, excess of iodine being carefully avoided, brilliant green spangles are deposited. The reaction is sufficiently delicate to form, according to Perrins, an excellent test of the presence of berberine. This iodo-compound polarizes light, and has other analogies with a similar quinine-salt termed Herapathite.

Berberine is not an official alkaloid, but the plants in which it occurs are used as medicinal agents in all parts of the world.

Process.—Berberine is readily extracted by boiling the raw material with water, evaporating the strained liquid to a soft extract, digesting the residue in alcohol, recovering the alcohol by distillation, boiling the residue with diluted sulphuric acid, filtering, and setting aside; the sulphate of berberine separates out, and may be purified by recrystallization from hot water. The alkaloid itself is obtained by shaking hydrate of lead with a hot aqueous solution of the sulphate of berberine (Procter).

Capsicine, or Capsicia.—M. Felletár obtained from capsicum-fruits (*Capsicum*, U. S. P.), which when ground form *Cayenne Pepper* or *African Pepper*, a volatile alkaloid having the smell of coniine. Thresh has obtained crystalline hydrochlorate and sulphate. The latter chemist has also succeeded in isolating the active principle of capsicum, which he has termed *capsaicin* ($C_9H_{14}O_2$), a crystalline, non-alkaloidal, excessively acrid substance. Its exact chemical character is not yet made out. (See also *Capsicin* in Index.)

Chelidonine ($C_{19}H_{17}N_3O_3$) and Chelerythrine ($C_{19}H_{17}NO_4$), the latter identical, apparently, with *sanguinarine*, are two alkaloids occurring in *Celandine* (*Chelidonium*, U. S. P.), associated with citric, malic, and chelidonic ($C_7H_4O_6$) acids.

Cocaine, or Cocaina ($C_{16}H_{19}NO_4$) is an alkaloid of *Erythroxylon coca* (*Erythroxylon*, U. S. P.), the leaves of which are said to be a powerful restorative to the human system.

Colchicine, or Colchicia, the active principle of *Colchicum autumnale* (*Colchici Radix; Colchici Semen*, U. S. P.), is said to be an alkaloid, though some investigators think it has more of the characters of a neutral substance and give it the name *Colchicin.* Teisel says it may be crystallized from chloroform. Hertel gives it the formula $C_{17}H_{23}NO_6$, and states that ebullition with acidulated water converts it into *colchicein*, $C_{17}H_{21}NO_5,2H_2O$. It needs further examination. The most active medicinal preparation is an extract made from the *fresh* seeds by digestion in large volumes of alcohol of at least 90 per cent., and subsequent digestion of the marc in hot water. The extracts left on evaporating the two fluids separately are to be carefully mixed (Mols).

Coniine, Conicine, Cicutine, Conia, or Conylia. Formula $C_8H_{17}N$ (Hofmann).—This alkaloid is a volatile liquid occurring in hemlock (*Conium maculatum*), in combination with an acid (malic?).

It is not official. According to Petit, its boiling-point is 170° C., and its density 0.846. It forms crystalline salts.

Process.—It may be obtained by distilling hemlock-fruit (*Conium*, U. S. P.) with water rendered slightly alkaline by caustic soda or potash, or by similarly treating the fresh juice of the leaves, The alkaloid is a yellow oily liquid floating on the water that distils over; by redistillation it is obtained colorless and transparent.

The salts of coniine have no odor, but when moistened with solution of an alkali yield the alkaloid, the strong smell of which, at once recalling hemlock, is characteristic. Extract of hemlock-leaves (*Conii Folia*, B. P.), to which solution of potash and boiling water have been added, forms the official Inhalation of Coniine (*Vapor Coniæ*, B. P.).

Tests.—Sulphuric acid turns coniine purplish-red, changing to olive-green, nitric acid a blood-red; perchloride of gold produces a yellowish-white precipitate, perchloride of platinum no precipitate, in aqueous solutions.

Hemlock also contains *methyl-coniine* $(C_8H_{14})''CH_3N_2$? (Kékulé and Van Planta), and *conhydrine*, $C_8H_{17}NO$.

According to Schiff, coniine, isomeric, at least, with the natural alkaloid, may be produced artificially by action of ammonia on butyric aldehyd and destructive distillation of the resulting compound.

CORYDALINE, CORYDALINA, or CORYDALIA, is an alkaloid obtained by Wenzell from "Turkey Corn," the tubers of *Dicentra* (*corydalis*) *formosa.*

DATURINE, or DATURIA. *Vide* HYOSCYAMINE.

DELPHININE, DELPHINE, or DELPHIA ($C_{21}H_{35}NO_2$) the poisonous alkaloid of Stavesacre, *Delphinium staphisagria* (*Staphisagria*, U. S. P.). The powdered seeds of the plant are employed to kill the *pediculi* of animals.

DITAMINE (Jobst and Hesse), the *Ditain* of Gruppe, is the alkaloid of "Dita," or bark of *Echites scholaris* or *Alstonia scholaris* (*Alstoniæ Cortex*, P. I.), a reputed febrifuge. Oberlin and Schlagdenhauffen state that the allied *Alstonia constricta* contains a crystalline alkaloid *alstonine* and uncrystallizable *alstonicine.* Alstonine seems to be allied to strychnine.

DUBOISINE, or DUBOISIA, is the name suggested by Gerrard for the alkaloidal active principle he extracted from *Duboisia myoporoides*, unless, as he adds, the body should prove to be atropine, to which it is, at all events, closely allied.

EMETINE, or EMETIA ($C_{30}H_{44}N_2O_8$, Glenard).—This alkaloid is the active emetic principle of the root of *Cephælis ipecacuanha* (*Ipecacuanha*, U. S. P.). It occurs in combination with ipecacuanhic acid. The nitrate is peculiarly slightly soluble in water (Lefort). In the *Pulvis Ipecacuanhæ et Opii*, U. S. P., or "Dover's Powder" (Powdered Ipecacuanha, 1 part; Powdered Opium, 1 part; and Sugar of Milk, 8 parts), minute division of the active ingredients is promoted by prolonged trituration with the sugar of milk, which is hard. The Indian substitute of Ipecacuanha is the dried leaf (*Tylo-*

phoræ Folia, P. I.) of *Tylophora asthmatica*. .Its active principle has not been satisfactorily isolated.

GELSEMINE, or GELSEMINIA ($C_{11}H_{19}NO_2$, Sonnenschein; $C_{12}H_{14}NO_2$, Gerrard), is the alkaloid of *Gelsemium sempervirens*, or *Carolina Yellow Jasmine* (*Gelsemium*, U. S. P.), in the tissues of which plant the *gelseminic acid* of Wormley and *æsculin* ($C_{30}H_{34}O_{19}$), the fluorescent glucoside of the Horse Chestnut and of many other plants, are also present.

HYOSCYAMINE, or HYOSCYAMIA ($C_{17}H_{23}NO_3$), a volatile alkaloid, occurs in the leaves (*Hyoscyamus*, U. S. P.), seed, and other parts of Henbane. According to Duquesnel, it is solid and crystalline. Its effect on the eye is similar to that of atropine. The researches of Buckheim point to the conclusion that hyoscyamine is the tropate of an alkaloid homologous with tropine (Sonnenschein). (See *Atropine*.)

Sulphate of Hyoscyamine, $(C_{17}H_{23}NO_3)_2,H_2SO_4$, is official (*Hyoscyaminæ Sulphas*, U. S. P.). It is yellowish-white.

Ladenburg also finds in henbane some *hyoscine*, a tropate of another alkaloid homologous with tropine.

The alkaloids which occur in *Datura Stramonium*, or Thorn-apple (*Stramonii Folia et Semen*, U. S. P.; *Dhatura: Datura alba; Daturæ Folia et Semina*, P. I.), and in *Duboisia myoporoides*, and formerly supposed to be distinct alkaloids, called respectively *Daturine* and *Duboisine*, are identical with hyoscyamine, and the latter is isomeric, if not identical, with atropine (Ladenburg.) Ordinary atropine also occurs in stramonium. Bees which sip from the flowers of stramonium are said to produce poisonous honey.

JERVINE, or JERVIA ($C_{30}H_{46}N_2O_3$) occurs in *Veratrum album*, White Hellebore, and *V. viride* (U. S. P.),* American White Hellebore, the root of which is officially recognized in Great Britain (*Veratri Viridis Radix*, B. P.). Its salts are much less soluble in water than those of veratrine. According to Bullock, *Veratrum viride* contains still another alkaloid, *veratroidine;* and, according to Mitchell, *Veratrum album* also contains an alkaloid which he terms *veratralbine*. Tobien gives the formula of jervine as $C_{27}H_{47}N_2O_8$, and of veratroidine as $C_{51}H_{78}N_2O_{16}$ or $C_{24}H_{37}NO_7$. According to Wright, *Veratrum album* contains jervine, $C_{26}H_{37}NO_3$; pseudojervine, $C_{29}H_{43}NO_7$; rubijervine, $C_{26}H_{43}NO_2$; veratralbine, $C_{28}H_{43}NO_5$; and traces of veratrine, $C_{37}H_{63}NO_{11}$. The same author finds *Veratrum viride* to contain jervine, pseudojervine, cevadine, $C_{32}H_{49}NO_9$, rubijervine, and traces of veratrine and veratralbine.

Juglandine is the name given by Tanret to an alkaloidal substance obtained from the leaves of the walnut, *Juglans regia*. In the root-bark of *Juglans cinerea*, or Butternut (*Juglans*, U. S. P.),

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* "The name *Green Hellebore* is sometimes applied to the drug, but it properly belongs to *Helleborus viridis* (p. 421), which is medicinal in some parts of Europe."—*Hanbury*.

Thiebaud found a bitter substance and an acid resembling chrysophanic.

Lobeline, or Lobelia.—A volatile fluid alkaloid first isolated from the dried flowering herb *Lobelia inflata* (*Lobelia*, U. S. P.) by Procter. In the pure state it smells slightly of the plant, but mixed with ammonia it emits a strong and characteristic smell of the herb. With acids it forms crystalline salts.

Lupuline is stated by Greismayer to be a liquid volatile alkaloid contained in hops (*Humulus lupulus*).

Nectandrine. *Vide* Beberine.

Nicotine, Nicotina, Nicotia, or Nicotylia, formula $C_{10}H_{14}N_2$, or $(C_5H_7)'''_2N_2$. This is also a volatile liquid alkaloid, forming the active principle of tobacco (*Nicotiana tabacum*), malate and citrate of nicotine being the forms in which it occurs in the leaf (*Tabacum*, U. S. P.). Its odor is characteristic; like coniine, it yields a precipitate with perchloride of gold; but, unlike that alkaloid, its aqueous solutions are precipitated yellowish-white by perchloride of platinum. It is not official. It is also contained in *pituri*, a drug "chewed by the natives of some parts of Australia as a stimulant narcotic."

Physostigmine, or Physostigma ($C_{30}H_{21}N_3O_4$).—An alkaloid contained in the Calabar bean (*Physostigma*, U. S. P.), the seed of *Physostigma venenosum* (Jobst and Hesse). A trace of it powerfully contracts the pupil of the eye; a small quantity is highly poisonous. Fraser also isolated another (but, possibly, the same) principle, and termed it *Eserine*, from Eserĕ, the name of this ordeal-poison at Calabar. *Salicylate of Physostigmine* is official (*Physostigminæ Salicylas*, U. S. P.), $C_{15}H_{21}N_3O_2,C_7H_6O_3$.

Pilocarpine is, apparently, the active principle of the diaphoretic and sialogogue *Jaborandi*, the leaflets of *Pilocarpus pinnatifolius* (*Pilocarpus*, U. S. P.). The occurrence of an alkaloid in this plant was first announced by Hardy, followed almost immediately by Byasson. A crystalline nitrate and hydrochlorate were first obtained by Gerrard. Kingzett gives the formula of pilocarpine as $C_{23}H_{34}N_4O_4$. The leaves also yield an essential oil, a terpene $C_{10}H_{16}$ (Hardy). Harnack and Meyer state that the true formula for pilocarpine is $C_{11}H_{16}N_2O_2$, and that its effects resemble those of nicotine, but that it readily yields another alkaloid, *jaborine*, which probably closely approaches pilocarpine in composition, but is allied to atropine in effects, and may be contained, ready formed, in *jaborandi*. One salt is official (*Pilocarpinæ Hydrochloras*, $C_{11}H_{16}N_2O_2,HCl$, U. S. P.).

Piperine, or Piperia (*Piperina*, U. S. P.) ($C_{17}H_{19}NO_3$), is a feeble alkaloid occurring in *white*, *black* (*Piper Nigrum*, U. S. P.), *long pepper* (*Chavica officinarum*, Mign.) and *cubeb pepper* (*Cubeba*, U. S. P.), associated with volatile oil and resin; to these three substances the odor, flavor, and acridity belong. Piperine is obtained on boiling white pepper with alcohol, and evaporating the liquid with solution of potash, which retains resin. Recrystallized from alcohol, piperine forms colorless prisms fusible at 212°. With acids and certain metallic compounds it forms salts, and distilled with strong alkali yields *piperidine* or *piperidia* ($C_5H_{10}HN$), an alkaloid of strong chemical properties, and *piperic acid* ($C_{12}H_{10}O_4$). According to Buckheim, the amorphous resin of the peppers is similar in constitution to piperine, alkalies breaking it up into piperidine and *chavicic acid*. *Pyrethrin* is also said to be a member of the series. The piperine of cubeb pepper is not to be confounded with *cubebin*, a neutral constituent having the formula $C_{33}H_{34}O_{10}$.

SANGUINARINE, or SANGUINARINA, is a colorless alkaloid obtained from the rhizome of *Sanguinaria canadensis* (*Sanguinaria*, U. S. P.), or Blood-root. Its salts have a red, crimson, or scarlet color. It appears to be identical with CHELERYTHRIN.

SOLANINE, or SOLANIA ($C_{43}H_{70}NO_{16}$).—An alkaloid said to exist in the Woody Nightshade or Bitter-sweet (*Solanum dulcamara*). The dried young branches of the plant are official (*Dulcamara*, U. S. P.). It occurs also in the shoots, and in minute amount in the skins of the tubers, of the potato (*Solanum tuberosum*). The alkaloid is only slightly soluble in water, alcohol, or ether; nitric acid colors it yellow; sulphuric acid produces at first a yellow, then a violet, and finally a brown coloration. It is said to be a conjugated compound of sugar with *solanidine* ($C_{25}H_{39}NO$). Geissler finds *dulcamarin* ($C_{22}H_{34}O_{10}$), a glucoside, to be the bitter constituent of *Solanum dulcamara*. A mixture of sulphuric acid and alcohol, or either selenic acid or selenate of sodium and sulphuric acid, colors solanine or solanidine a dark red.

SPARTEINE, or SPARTEIA ($C_{15}H_{26}N$), is a poisonous volatile alkaloid occurring in Broom-tops (*Scoparius*, U. S. P.). Its discoverer, Stenhouse, considers that the diuretic principle of broom is *scoparin*, a non-poisonous body. Mills has obtained ethyl-sparteine ($C_{15}H_{25}C_2H_5N$) and diethyl-sparteine ($C_{15}H_{24}C_2H_5C_2H_5N$).

SPIGELINA.—According to Dudley, this is a volatile alkaloid and active principle of *Spigelia marilandica*, or Pink-root (*Spigelia*, U. S. P.).

THEINE, THEIA, or CAFFEINE ($C_8H_{10}N_4O_2 + H_2O$). This alkaloid (*Caffeina*, U. S. P.) occurs in tea, 1 to 4 per cent., coffee, .5 to 2 per cent., Maté or Paraguay tea, .2 to 2 per cent., guarana (*Guarana*, U. S. P., "a dried paste prepared from the crushed or ground seeds of *Paullinia sorbilis*"), 5 per cent., and the kola-nut. Infusions and preparations of these vegetable products are used, chiefly as beverages, by three-fourths of the human race. It is remarkable that the instinct of man, even in his savage state, should have led him to select, as the bases of common beverages, just the four or five plants which out of many thousands are the only ones, so far as we know, containing theine. Theine is volatile. Considerable quantities may be collected by condensing the vapors evolved during the roasting of coffee on the large scale. The infusion of tea, from which astringent and coloring matters have been precipitated by solution of subacetate of lead, and which has been evaporated to a small bulk, yields a precipitate of theine on the addition of a strong solution of carbonate of potassium. It may be crystallized from alcohol or by sublimation. Theine forms salts with the stronger acids; they are decomposed by water.

Test.—Concentrated nitric acid, or, better, a mixture of chlorate of potassium and hydrochloric acid, rapidly oxidizes theine, forming compounds which with ammonia yield a beautiful purple-red color, resembling the murexid obtained under similar circumstances from uric acid; the oxidation must not be carried too far. Theine boiled with caustic potash yields methylamine (CH_3HHN), the vapor of which has a peculiar characteristic odor.

The chemical action of theine on the system is not yet made out. It is probably a pure stimulant.

Veratrine, or Veratria (*Veratrina*, U. S. P.) ($C_{32}H_{50}NO_9$, Schmidt and Koppen; $C_{52}H_{86}N_2O_{15}$, Weigelin).—This alkaloid occurs in *Cevadilla* (*Sabadilla*, B. P.; the seeds of *Asagrea officinalis*, Lindley, termed *Sabadilla officinarium* by Brandt, and *Veratrum officinale* by Schlecht). It is also said to occur in the leaves of *Sarracenia purpurea.* According to Weigelin, Cevadilla contains two isomeric varieties of veratrine, the one soluble, the other insoluble, in water. There are also present *Sabadilline* ($C_{41}H_{66}N_2O_{13}$) and *Sabatrine* $C_{51}H_{86}N_2O_{17}$). The veratrine of trade contains the two latter alkaloids (Weigelin). A mere trace of veratrine brought into contact with the mucous membrane of the nose causes violent fits of sneezing. These alkaloids, and those from the different species of Veratrum, are evidently very closely allied. Wright and Luff, by the use of tartaric acid, a solvent less likely than the strong acids to decompose alkaloids, extract from Cevadilla, Veratrine, $C_{37}H_{53}NO_{11}$; Cevadine, $C_{32}H_{49}NO_9$; and Cevadilline, $C_{34}H_{53}NO_8$.

The official process for the preparation of the alkaloid (*Veratria*, B. P.) consists in exhausting the disintegrated cevadilla-seeds by alcohol, recovering most of the spirit by distillation, pouring the residue into water, by which much resin is precipitated, filtering, and precipitating the veratrine from the aqueous solution by ammonia. It is purified by washing with water, solution in dilute hydrochloric acid, decolorization of the liquid by animal charcoal, reprecipitation by ammonia, washing, and drying. The U. S. P. (1870) process is similar, but includes treatment of the first crude veratrine by diluted sulphuric acid and precipitation of alkaloid by magnesia.

Unguentum Veratrinæ, U. S. P., contains 4 per cent. of the alkaloid.

QUESTIONS AND EXERCISES.

694. How is Aconitine prepared?

695. Give the strength of the official preparations of Atropine.

696. Describe the properties of atropine.

697. What is the active principle of stramonium?

698. Mention pharmacopœial substances containing beberine and berberine respectively.

699. Give the characters of beberine.

700. In what does nectandrine differ from beberine?
701. Mention the characteristics of coniine.
702. What is the active principle of Ipecacuanha?
703. Name the alkaloid of Tobacco.
704. Give the name and properties of the active principle of Calabar Bean.
705. What are the sources of piperine?
706. Whence is theine obtained?
707. Describe the preparations of veratrine.
708. State the properties of veratrine.

BITTER OR TONIC SUBSTANCES, Etc.

The following articles, employed medicinally in such forms as Decoction, Extract, Infusion, Tincture, etc., contain active principles which have not yet been thoroughly examined. Some of these principles have been isolated, and a few have been obtained in the crystalline condition, but their constitution has not been sufficiently well made out to admit of the classification of the bodies either among alkaloids, glucosides, acids, or other well-marked principles:—

Andrographis Caules et Radix, P. I., from *Andrographis paniculata*, Kariyat.

Anthemidis flores.

Apocynum. Canadian Hemp.

Asclepias tuberosa. Pleurisy-root (Asclepedin).

Aurantii cortex (Hesperidin).

Azadirachtæ Cortex et Folia, P. I., from *Azadirachta indica*, Ním or Margosa. (A resin; $C_{36}H_{50}O_{11}$. Broughton.)

Baptisia tinctoria. Wild Indigo. Alkaloid? B. L. Smedley, Greene.

Bonducella semina, P. I., from *Cæsalpinia* (*guilandina*) *bonducella.* Bonduc-seeds or nickar-nuts.

Buchu folia.

Calendula officinalis. Marigold. (Calendulin, Stoltze.)

Calotropis Cortex, P. I., from *Calotropis procera* and *C. gigantea.* Mudar.

Canellæ albæ cortex.

Cascarillæ cortex (Cascarillin, $C_{12}H_{11}O_4$).

Caulophyllum thalictroides. Blue cohosh. Alkaloid?

Cimicifuga (*Actea*) racemosa (Cimicifugin?). Black snake-root.

Cuspariæ cortex. Angustura-bark (Cusparin).

Cypripedium pubescens (Cypripedin?). Ladies' Slipper.

Euonymus atropurpureus. Wahoo-bark (Euonymin?).

Eupatorium perfoliatum. Thoroughwort or Boneset.

Grindelia robusta. Resin?

Gulancha (*Tinosporæ Radix et Caules*, P. I.).

Gynocardiæ semina, from *Gynocardia odorata* (*Chaulmugra*, P. I.).

Hamamelis virginica. Witch-hazel.

Hedeoma pulegioides. American pennyroyal.

Hydrocotyles folia, P. I., from *Hydrocotyle asiatica.* Indian pennywort.

Iris versicolor. Blue flag (Iridin or Irisin?).

Lactuca (Lactucin, etc.). The milk-juice, dried, yields *Lactucarium*, U. S. P.

Lappa, U. S. P., *Arctium lappa*, *Lappa officinalis.* Burdock.

Lupulus.
Magnolia. Swamp Sassafras or Beaver Tree.
Marrubium. Horehound. Marrubein, a crystalline bitter substance (Mein).
Maticæ folia. Matico.
Melia Azedarach (Resin, Jacobs).
Pepo. The seed of *Cucurbita pepo.* A remedy for tapeworm.
Phytolacca bacca et Radix. Poke, berry and root. Phytolaccin, a crystalline substance (Claassen).
Quassiæ lignum (Quassin, $C_{10}H_{12}O_3$).
Scutellaria. Skullcap.
Serpentaria. Virginia Snake-root.
Stillingia. Queen's Root.
Soymidæ Cortex, P. I. Rohun Bark, from *Soymida febrifuga.*
Taraxaci radix (Taraxacin).
Toddaliæ radix, P. I.
Triticum repens. Rhizome of couch-grass.
Veronica virginica, or *Leptandra virginica.* Culvers root; *Leptandra,* U. S. P. (Leptandrin?).
Viburnum. Black haw. (*Viburnin*).

AMYLACEOUS AND SACCHARINE SUBSTANCES.

STARCH.

Formula $C_6H_{10}O_5$; possibly $C_{72}H_{120}O_{60}$.

Processes.—Rasp or grate, or, with a knife, scrape, a portion of a clean raw potato, letting the pulp fall on to a piece of muslin placed over a small dish or test-glass, and then pour a slow stream of water over the pulp; minute particles or *granules* of starch pass through the muslin and sink to the bottom of the vessel, fibrous matter remaining on the sieve. This is potato-starch. Even diseased potatoes furnish good starch by this method. Wheat-starch (*Amylum,* U. S. P.) may be obtained by tying up some flour in a piece of calico and kneading the bag in a slow stream of water flowing from a tap, the washings running into a deep vessel, at the bottom of which the white starch collects; the sticky matter remaining in the bag is *gluten.* The *blue starch* of the shops is artificially colored with smalt or indigo to neutralize the yellow tint of recently washed linen; it should not be used for medicinal purposes. Starch dried in mass splits up into curious columnar masses, resembling the basaltic pillars of Fingal's Cave in Staffa or those of the Giant's Causeway in the North of Ireland. The cause of the phenomenon, which may also be seen in grain-tin, is not conclusively known.

Gluten is the body which gives tenacity to dough and bread. It seems to be a mixture of vegetable fibrin, vegetable casein, and an albuminous matter termed glutin. These substances and gluten itself are closely allied; each contains about 16 per cent. of nitrogen. *Wheaten Flour* (*Farina Tritici,* B. P.) contains about 72 per cent. of starch and 11 of gluten, as well as sugar, gum, fine bran, water, and ash. The compactness of barley, well seen in Husked or Pearl Barley (*Hordeum Decorticatum*, B. P.), is said to be due to the large amount of vegetable fibrin present. During germination the fibrin is destroyed; hence, probably, the cretaceous character of malt. *Oatmeal* is very rich in albumenoid or flesh-forming constituents, containing nearly 16 per cent. *Sago* is granulated starch from the Sago Palm. *Tapioca* is granulated starch from the Bitter Casava. The white translucent grains known as Rice are the husked seeds of *Oryza sativa.* Rice (*Oryza*) and the Flour of Rice, or Ground Rice (*Oryza Farina*), are official in the Pharmacopœia of India. Rice is quite a staple article of food in tropical coutries. Ground rice resembles flour of wheat in composition, but contains from 85 to 90 per cent. of starch.

Microscopical Examination of Starches.—All kinds of starch afford the blue color with iodine, showing their chemical similarity. Physically, however, the granules of different starches differ from each other; hence a careful microscopical examination of any starch, or of any powder or vegetable tissue containing starch, enables the observer to state, with a high degree of probability, the source of the starch, either at once if he has much experience, or after comparing the granules in question with authentic specimens. A glance at the accompanying eight engravings* (Figs. 41 to 48) of common starches will show to what extent different starch-granules naturally differ in size, shape, general appearance, distinctness and character of the rugæ, and position of the more or less central point or hilum. While from different starches individual granules may be picked out which much resemble each other, the appearance of each starch as a whole is fairly characteristic. That is to say, each *group* of granules differs in one, two, or several characters from similar *groups* of granules of other starches.

A quarter-inch object-glass will commonly suffice for the microscopical examination of starch. A very little of the starch is mixed on a glass slide with a drop of water, a piece of thin covering-glass being placed on the drop and gently pressed, so as to provide a very thin layer for observation. Instead of water diluted spirit of wine, diluted glycerin, turpentine, or other essential oil, Canada balsam, and other fluids, may be used in cases where the markings or other appearances are not well defined. The illumination also of the granules may be varied, the light being reflected or transmitted, concentrated or diffused, white or colored, polarized or plain. Polarized light is especially valuable in developing differences and in intensifying the effects of obscure markings. By polarized light the granules of potato-starch appear as if traversed by a black cross: wheat-starch granules and many others also peculiarly and characteristically influence polarized light. Distinctive characters will sometimes present themselves only when the granules are made to roll over in the fluid in which they have been temporarily mounted or when the

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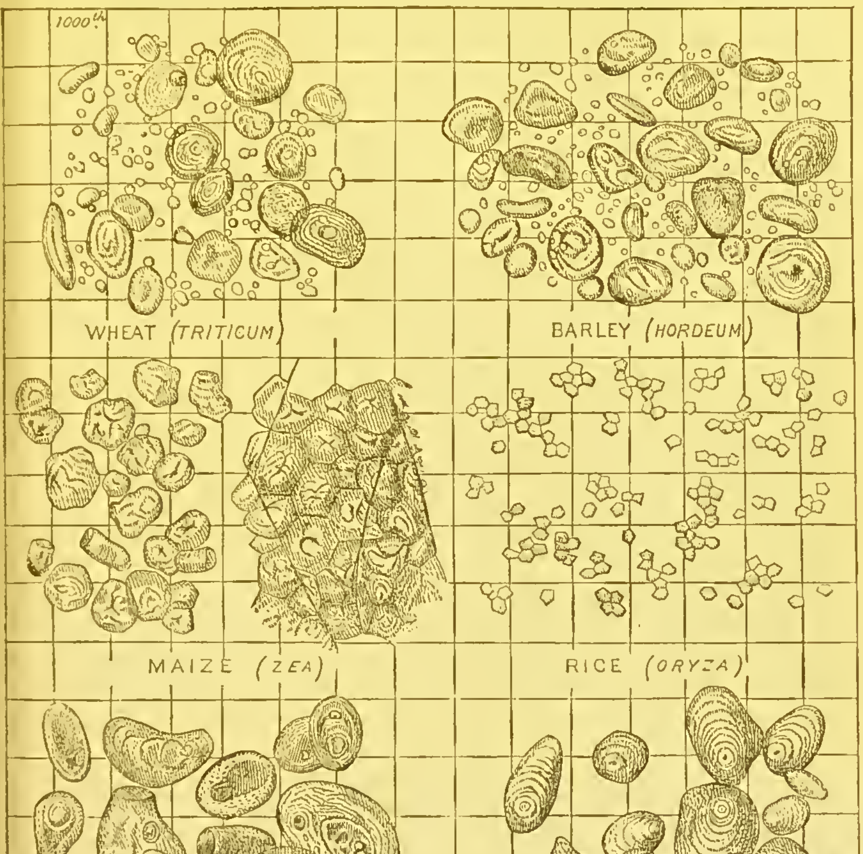
* By permission of Messrs. Longmans & Co. these engravings have been copied, with very few modifications, from the plates in two of the three volumes of the original edition of Pereira's *Materia Medica.*

STARCHES

(Magnified 250 diameters).

Figs. 41 to 48.



slide is gently warmed. Starches which have already been subjected to the influence of heat, partly as in sago or tapioca, or almost entirely as in bread, will of course differ in appearance from granules of the same starch before being dried, cooked, or torrefied. The characters of a starch will also somewhat vary according to the age and condition of the plant yielding it.

For plates and descriptions of the characters of other starches occurring in plants used for medicinal purposes, the reader is referred to works on Materia Medica and to the indexes of Journals of Pharmacy, as well as to general works and magazines on microscopy. For engravings of starch granules *in situ*, *vide* Berg's *Anatomischer Atlas*, published by Gaertner, Berlin.

The student may place fair confidence in the accompanying illustrations and in most of the published engravings of starch granules; but in microscopical analyses of importance the worker should, if possible, himself obtain actual specimens of starches for comparison from the respective seeds, fruits, and other tissues.

Inulin ($C_6H_{10}O_5$) is a white powder apparently occupying the place of starch in the roots of many plants, especially those of the natural order *Compositæ*. Twenty to forty-five per cent. has been obtained from elecampane (*Inula helenium*). It is also contained in the dahlia, colchicum, arnica, dandelion, chicory, etc. It is soluble in boiling water, nearly all being redeposited on cooling. Iodine turns it yellow. Long ebullition converts it into a kind of gum.

Lichenin ($C_6H_{10}O_5$) is a white starch-like powder largely contained in many lichens—Iceland "Moss," *Cetraria islandica*, and many others. It is soluble in boiling water, and the fluid gelatinizes on cooling. It may be precipitated from its aqueous solution by alcohol. With iodine it gives a reddish-blue color.

Mucilage of Starch.—Mix two or three grains of starch with first a little and then more water, and heat to the boiling-point; mucilage of starch (*Mucilago Amyli*, B. P.) results. 1 part of starch to 200 of water gives *Gelatinized Starch*, U. S. P.

This mucilage or paste is not a true solution; by long boiling, however, a portion of the starch becomes dissolved. In the latter case the starch probably becomes somewhat altered.

Chemical Test.—To some of the mucilage add a little free iodine; a deep blue color is produced.

This reaction is a very delicate test of the presence of either iodine or starch. The starch must be in the state of mucilage; hence in testing for starch the substance supposed to contain it must be first boiled in water. The solutions used in the reactions should also be cold or nearly so, as the blue color disappears on heating, though it is partially restored on cooling. The iodine reagent may be iodine-water or tincture of iodine. In testing for iodine its occurrence in the free state must be insured by the addition of a drop, or even less, of chlorine-water. Excess of chlorine must be avoided, or chloride of iodine will be formed, which does not color starch.

The so-called *Iodized Starch* (*Amylum Iodatum*, U. S. P.), or *iodide of starch* (Starch, 95; Iodine, 5) scarcely merits the name of a chemical compound, the state of union of its constituents being feeble. Substances that attack free iodine remove that element from iodide of starch. The alkalies, hydrosulphuric acid, sulphurous acid, and other reducing reagents destroy the blue color.

Composition of Starch Granules.—Starch granules consist mainly of *granulose*, soluble in cold water and giving an indigo-color with iodine, and *starch cellulose*, insoluble in water and giving with iodine a dirty-yellow color. The starch cellulose forms an external coating upon the granule, and also exists mixed with the granulose inside the granule. If this coating be broken by mechanical means, the continued application of cold water will remove all the granulose, leaving the cellulose insoluble. By the action of diastase, ptyalin, and other ferments, and by other means, the granulose may be converted into sugar and dextrin, leaving the starch cellulose unacted upon.

DEXTRIN.—Mix a grain or two of starch with about half a test-tubeful of cold water and a drop or two of sulphuric acid, and boil the mixture for a few minutes; no mucilage is formed, and the liquid, if sufficiently boiled, yields no blue color with iodine; the starch has become converted into *dextrin* and some sugar. Dextrin is also produced if starch is maintained at a temperature of about 320° F. for a short time. Dextrin is now largely manufactured in the latter way, and a paste of it used by calico-printers as a vehicle for colors; it is termed *British gum*. The change may also be effected by *diastase*, a peculiar ferment existing in malt. Mix two equal quantities of starch with equal amounts of water, adding to one a little ground malt, then heat both slowly to the boiling-point; the mixture without malt thickens to a paste or pudding, that with malt remains thin, its starch having become converted into dextrin and a sugar termed maltose.

Diastase is probably a mixture of the coagulable albumenoids. It is so named from *διάστασις* (*diastasis*), *separation*, in allusion to the separation, or rather alteration, it effects among the constituent atoms of the molecule of starch. This function is shared by the saliva, pancreatic juice, bile, and the intestinal and other juices. The function is destroyed when the albumenoids are coagulated by a temperature of from 80°–81° C.

The Action of Diastase upon Starch.—Diastase has scarcely any action upon unbroken starch granules. The granules must be ruptured by gelatinization with heat and moisture or in some other way. When a solution containing diastase, such as a cold-water infusion of malt, be allowed to act upon gelatinous starch or starch paste at 60° to 70° C., liquefaction occurs. It is possible to operate so that when liquefaction has taken place the solution shall give no reaction for sugar or dextrin. If this solution be concentrated and allowed to cool, a glistening white precipitate of soluble starch falls. Soluble starch is probably the result of the partial decomposition of the more complex molecule of granulose or gelatinous starch. The next step in the action of diastase upon gelatinous starch is the breaking down of the soluble starch molecule into dextrin and a sugar called maltose. At least ten dextrins are successively produced, each simpler than the one preceding it, the proportion of maltose being correspondingly increased. The dextrins first produced give a red or brown color with iodine, while those last produced, and having a simpler molecule, give no color with iodine. The final reaction may be expressed thus:—

$$\underset{\text{Soluble starch.}}{10(C_{12}H_{20}O_{10})} + 8H_2O = \underset{\text{Maltose.}}{8(C_{12}H_{22}O_{11})} + \underset{\text{Dextrin.}}{2(C_{12}H_{20}O_{10})}$$

The dextrins are distinguished by their rotary power, their reducing action on cupric salts, and in other ways.

Starch heated with glycerin is converted into the soluble variety. The latter may be precipitated from an aqueous solution by strong alcohol. A strong solution in water gradually gelatinizes, owing to reconversion into insoluble starch (Zulkowsky).

The Action of Dilute Acids upon Starch.—Dilute acids act upon gelatinous starch in the same way as diastase, except that the final product is glucose.

Malt (the word malt is said to be derived from the Welsh *mall*, soft or "rotten") is simply barley which has been softened by steeping in water, allowed to germinate slightly, and further change then arrested by the application of heat in a kiln. During germination the gluten breaks up and yields a glutinous substance termed vegetable gelatin, diastase, and other matters. To the vegetable gelatin is due much of the "body" of well-malted and slightly-hopped beer; it is precipitated by tannic acid, hence the thinness of ale (pale or bitter) brewed with a large proportion of hop or other materials containing tannic acid. A portion of the diastase, reacting on the starch of the barley, converts it into dextrin, and, indeed, carries conversion to the further stage of grape-sugar, as will be explained immediately. The temperature to which the malt is heated is made to vary, so that the sugar of the malt may or may not be partially altered to a dark-brown coloring-material; if the temperature is high, the malt is said to be *high-dried*, and is used in porter-brewing; if low, the product is of lighter color, and is used for ale (*Maltum*, U. S. P., "not darker than pale amber"). The diastase remaining in malt is still capable of converting a large quantity of starch into dextrin and sugar (maltose); hence the makers or distillers of the various spirits operate on a mixture of malted and unmalted grain in preparing liquors for fermentation.

Extract of malt is an evaporated infusion of malt. Taken with food, its diastase aids in the conversion of starch into a variety of sugar termed maltose and dextrin, and, *pro tanto*, assists enfeebled digestive powers.

$$\underset{\text{Starch.}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_5H_{10}O_5}$$

As diastase loses this power at a temperature above 150° F., that degree should not be exceeded in evaporating the infusion; indeed, if the dissolved albumenoid matters are to be retained, the evaporation should be conducted at 120° F. (For a method of estimating the strength of extract of malt, see a paper by Dunstan and Dimmock, *Pharm. Journ.*, March 8, 1879.)

Gum is a frequent constituent of vegetable juices, existing in large quantity in several species of acacia. According to Frémy, gum is a calcium salt, sometimes partially a potassium salt of the *gummic* or *arabic* radical. The formula of gummic acid is said to be $H_2C_{12}H_{18}O_{10},H_2O$. Gum differs from dextrin in yielding mucic acid when oxidized by nitric acid. *Cerasin*, or *cherry-tree gum*, is an insoluble modification of acacia gum. *Bassorin*, *traganthin* or *adraganthin* ($C_{12}H_{20}O_{10}$), is a form of gum which is insoluble in water, but absorbs a large quantity of that liquid and forms a gelatinoid mass. It occurs largely in Tragacanth, combined, like arabin, with calcium. *Pectin*, or *vegetable jelly* ($C_{23}H_{40}O_{28},4H_2O$), is the body which gives to expressed vegetable juices the property of gelatinizing. It forms the chief portion of Irish or Carrageen "Moss," *Chondrus crispus*, (*Chondrus*, U. S. P.). *Ceylon* "*Moss*" (*Gracillaria lichenoides* and *G. confervoides*, P. I.) contains from one-third to three-fourths of vegetable jelly.

The mucilage of marshmallow-root (*Althea officinalis*) (*Althea*, U. S. P.), and of linseed or common flaxseed (*Linum usitatissimum*), is a gum-like substance containing much mineral matter. It is the basis of the infusions termed *mallow-tea* and *linseed-tea*. Somewhat similar mucilage occurs in infusion of Bael; it is also largely yielded by the seeds of the Quince (*Cydonium*, U. S. P.) and by ordinary Elm-Bark (*Ulmi Cortex*, B. P.), as well as by the bark of the Red or Slippery Elm (*Ulmi Fulvæ*) (*Ulmus*, U. S. P.). *Salep*, the powdered dried tubers of many species of *Orchis*, contains a large quantity of such matter. *Squill* also. The Indian *Okro* (*Hibisci Capsulæ*, P. I., from *Hibiscus esculentus*) and *Ispaghúl*- or *Spogel*-seeds (*Ispaghulæ semina*, P. I., from *Plantago ispaghula*) also appear to contain a considerable quantity. In *Sassafras-Pith* (*Sassafras Medulla*, U. S. P.) starch and much mucilage occur.

Isomerism—Allotropy—Polymorphism.

The composition of dextrin is represented by the same formula as that of starch, namely $C_6H_{10}O_5$, for it has the same percentage composition as starch. Inulin (p. 404) and cellulose have also a similar formula. There are many other bodies similar in centesimal composition, but dissimilar in properties; such substances are termed *isomeric* (*ἴσος*, *isos*, equal, and *μέρος*, *meros*, part), and their condition is spoken of as one of *isomerism*. There is sometimes good reason for doubling or otherwise multiplying the formula of one of two *isomers*, *isomerides*, or isomeric bodies. Thus a molecule of olefiant gas (ethylene), the chief illuminating constituent of coal-gas, is represented by the formula C_2H_4, while a molecule of amylene, an anæsthetic liquid hydrocarbon, obtained from amylic alcohol, though having the same percentage composition as olefiant gas, is represented by the formula C_5H_{10}; for amylene, when gaseous, is about twice and a half as heavy as ethylene, and must contain, therefore, in each molecule, twice and a half as many *atoms*, for (law of Avogadro) these equal volumes must contain equal numbers of molecules: its formula is, consequently, constructed to represent those proportions. (Read again pages 38–42.) This variety of isomerism is termed *polymerism* (from πολὺς, *polūs*, many or much, and μέρος, part). Metastannic acid (*vide* p. 239) is a polymeric variety or *polymeride* of stannic acid. An illustration of a second variety of isomerism is seen in the case of cyanate of ammonium and urea, bodies already alluded to in connection with Cyanic Acid. These and several other pairs of chemical substances have dissimilar properties, yet are similar not only in elementary composition and in the centesimal proportion of the elements, but also in the fact that each molecule possesses the same number of atoms. But the reactions of these bodies indicate the probable nature of their construction; and this is shown in their formulæ by the disposition of the symbols. Thus cyanate of ammonium is represented by the formula $CNONH_4$, urea by CON_2H_4. Such bodies are termed *metameric* (from μετὰ, *meta*, a preposition denoting change, and μέρος), and their condition spoken of as one of *metamerism*. Acetate of ethyl (p. 297) is metameric with butyric acid (p. 360), for they have the same percentage composition and their vapors have the same specific gravity, and each therefore might be represented by the formula $C_4H_8O_2$; but their properties warrant us in assuming that their atoms occupy different positions in the two molecules—justify us in giving $C_2H_5C_2H_3O_2$ as a picture of a molecule of acetate of ethyl, and $HC_4H_7O_2$ as a picture of a molecule of butyric acid. Acetate of methyl ($CH_3C_2H_3O_2$), propionic acid ($HC_3H_5O_2$), and formate of ethyl ($C_2H_5CHO_2$) are isomers of the metameric variety, or *metamerides;* also quinine and quinidine, cinchonine and cinchonidine, and many of the volatile oils, etc. The isomerism of starch and dextrin may be of a polymeric or of a metameric character, but we do not yet know which, and must therefore at present give them identical formulæ. Substances similar in composition and constitution, yet differing in properties, are termed *allotropic* (ἄλλος, *allos*, another; τρόπος, *tropos*, condition). Thus ordinary phosphorus, kept at a temperature of about 450° F. in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500° F. (red or amorphous phosphorus). A black allotropic variety of phosphorus is known. There are also three *allotropes* of carbon, which are respectively crystalline, graphitic, and amorphous. Sulphur may be obtained in the viscous as well as in the hard, brittle condition. Another illustration of *allotropy* is seen in the varieties of tartaric acid, which have different optical properties, but otherwise are identical: they are in neither of the above-mentioned states of isomerism, but are allotropic modifications of the same substance. Occasionally one and the same substance crystallizes in two distinct forms; its state is then described as one of *polymorphism* (*πολὺς*, *polūs*, many; *μορφὴ*, *morphē*, form). Sulphur is polymorphous. It crystallizes by slow cooling in (1) prismatic crystals of sp. gr. 1.98, while in nature it occurs in (2) octahedra of sp. gr. 2.07. Melted and poured into water, sulphur takes up the form of (3) caoutchouc, of sp. gr. 1.96. These differences warrant the statement that sulphur occurs in three distinct allotropic conditions. Possibly such conditions result from the association of different numbers of atoms in the molecule of the element; that is, allotropic bodies may simply be *physically polymeric* or in some other way be mere *physical isomerides*.

Cellulin, or cellulose, the woody fibre of plants, familiar in the nearly pure state under the forms of "cotton-wool" (*Gossypium*, B. P. and U. S. P., "hairs of the seed of various species of Gossypium"), paper, linen, and pith, is another substance isomeric, probably polymeric, with starch. Lignin is a closely allied body lining the interior of woody cells and vessels. By the action of nitric acid of various strengths on cellulin, peroxide of nitrogen (NO_2) is substituted for one, two, or three atoms of hydrogen—mono-, di-, or trinitrocellulin being formed:—

$$\underset{\text{Cellulin.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Mononitrocellulin.}}{C_6\left\{\begin{matrix}H_9\\NO_2\end{matrix}\right\}O_5} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Cellulin.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Dinitrocellulin.}}{C_6\left\{\begin{matrix}H_8\\2NO_2\end{matrix}\right\}O_5} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\text{Cellulin.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3HNO_3} = \underset{\text{Trinitrocellulin.}}{C_6\left\{\begin{matrix}H_7\\3NO_2\end{matrix}\right\}O_5} + \underset{\text{Water.}}{3H_2O}$$

Trinitrocellulin is highly explosive gun-cotton; dinitrocellulin is not sufficiently explosive for use instead of gunpowder; mononitrocellulin is scarcely at all explosive. The three movable atoms of hydrogen in cellulin may be displaced by bodies other than peroxide of nitrogen.

Dinitrocellulin (*Pyroxylinum*, U. S. P.).—Mix 6 parts of sulphuric acid and 5 of nitric in an earthenware mortar. When cooled to about 32° C. (90° F.), immerse 1 part of cotton-wool in the mixture, and stir it with a glass rod so that it is thoroughly and uniformly wetted by the acids. Macerate for about ten hours, or until a sample washed with water and then with alcohol is soluble in a mixture of 1 vol. of alcohol and 3 of stronger ether. Transfer the cotton to a vessel containing a considerable volume of water, stir it rapidly and well with a glass rod, decant the liquid, pour more water upon the mass, agitate again, and repeat the affusion, agitation, and decantation until the washing ceases to give a precipitate with chloride of barium or to taste acid. Drain the product on filtering-paper, and dry in a water-bath.

Pyroxylin may also be made by soaking 7 parts of white filtering-paper, which has been washed in hydrochloric acid and dried, in a mixture of 140 parts of sulphuric acid (sp. gr. 1.82) and 70 of nitric acid (1.37) for three hours, and well washing the product (Guichard). *Mononitrocellulin* and *trinitrocellulin* are insoluble in a mixture of alcohol and ether; *dinitrocellulin* or *pyroxylin* is soluble, the solution forming ordinary collodion (*Collodium*, U. S. P.). The official proportions are 4 parts of pyroxylin dissolved in a mixture of 70 of stronger ether and 26 of alcohol. After digesting for a few days the liquid is decanted from any insoluble matter and preserved in a well-corked bottle. It is "a colorless, highly inflammable liquid with ethereal odor, which dries rapidly upon exposure to the air, and leaves a thin, transparent film insoluble in water or rectified spirit." Flexible collodion (*Collodium Flexile*, U. S. P.) is a mixture of collodion (92 parts), Canada turpentine, (5 parts), and castor oil (3 parts). A Styptic Collodion (*Collodium Stypticum*) is also official.

QUESTIONS AND EXERCISES.

709. How is wheat-starch or potato-starch isolated?
710. Define gluten and glutin.
711. Enumerate the proximate principles of wheaten flour.
712. Is starch soluble in water?
713. Which is the best chemical test for starch?
714. Distinguish physically between the varieties of starch.
715. Into what compound is starch converted by heat?
716. What occurs when a mixture of starch and water is allowed to flow into hot diluted sulphuric acid?
717. If equal amounts of starch and water be heated, one containing a small quantity of ground malt, what effects ensue?
718. Write a short article on the chemistry of "malting."
719. What is the nature of gum-arabic, and how is it distinguished from "British Gum"?
720. Explain *isomerism*, giving several illustrations.
721. Give examples of polymeric bodies.
722. State the formula of a body metameric with urea.
723. Define *allotropy* and *polymorphism*, giving illustrations.
724. What form of cellulin is official?
725. Mention the properties of the products of the action of nitric acids of various strengths on cellulin.
726. How is pyroxylin prepared?

SUGARS.

Sucrose, or cane-sugar, $C_{12}H_{22}O_{11}$. Maltose, $C_{12}H_{22}O_{11}$. Lævulose, or inverted sugar, $C_6H_{12}O_6$. Dextrose, glucose, or grape-sugar, $C_6H_{12}O_6,H_2O$. Lactose, or milk-sugar, $C_{12}H_{22}O_{11},H_2O$.

Artificial Formation of Grape-sugar from Cane-sugar—Tests *for Sugar.*—Dissolve a grain or two of common cane-sugar in water. To a portion of this solution placed in a test-tube add more water, two or three drops of solution of sulphate of copper, a considerable quantity of solution of potash or soda (enough to turn the color of the liquid from a light to a dark blue), and heat the mixture to the boiling-point; no obvious immediate change occurs. To another portion of the syrup add a drop of sulphuric acid, and boil for ten or twenty minutes, then add the copper solution and alkali, and heat as before; a yellowish-red precipitate of cuprous oxide (Cu_2O) falls. This test is exceedingly delicate.

The above reaction is due to the conversion of the *cane-sugar* ($C_{12}H_{22}O_{11}$) into *inverted sugar*, or *lævulose*, $C_6H_{12}O_6$ (so called because its solution causes left-handed rotation of a ray of polarized light, cane-sugar having an opposite effect), and *grape-sugar*, $C_6H_{12}O_6,H_2O$, by the influence of the sulphuric acid, and to the reducing action of the inverted sugar on the cupric solution. The formation of a precipitate immediately, without the action of acid, shows the presence of the latter sugars—its formation only after ebullition with acid indicating, in the absence of starch or dextrin, cane-sugar. In this reduction process the sugar is oxidized and broken up into several substances, but the exact nature of the reaction has not been ascertained.

Dextrin also reduces the copper salt to suboxide, unless its solution is cold and very dilute. It does not, however, so act on a solution of cupric acetate acidified with acetic acid, while glucose produces with this liquid the usual red cuprous precipitate (Barfoed).

Cane-sugar, or *sucrose* (*Saccharum*, U. S. P.), is a frequent constituent of vegetable juices. Thus it forms the chief portion of cassia-pulp (*Cassia Fistula*, U. S. P.), is contained in the carrot and turnip, but is most plentiful in the sugar-cane; much, however, is now obtained from the sugar-maple and beet-root. On the evaporation of the juice common *brown* or *moist sugar* crystallizes out; this, by re-solution, filtration through animal charcoal, evaporation to a strong syrup, and crystallization in moulds, yields the compact crystalline conical loaves known in trade as *loaf-sugar*. From a slightly less strong syrup, slowly cooled, the crystals termed *sugar candy* are deposited, white or colored according to the color of the syrup.

Maltose, $C_{12}H_{22}O_{11}$.—This crystallizable sugar is formed, together with dextrin, when diastase or dilute acids act upon starch. In the case of diastase it is the ultimate product, but the dilute acids may convert it into dextrose. It reduces cupric salts, but to a less extent than dextrose. It differs also from dextrose in its optical activity.

Inverted Sugar, or *Lævulose*, is uncrystallizable. It is found in the grape, fig (*Ficus*, U. S. P.) cherry, and gooseberry; both grape-sugar and fruit-sugar in the strawberry, peach, plum, etc. Fruit-sugar reduces cupric salts and ammonio-nitrate of silver.

Grape-sugar, *glucose* (from γλυκὺς, *glucūs*, sweet), or *dextrose*, is often seen in the crystallized state in dried grapes or raisins and other fruits; it is also the variety of sugar met with in diabetic urine. Its crystalline character is quite distinct from that of cane-sugar, the latter forming large four- or six-sided rhomboidal prisms, while grape-sugar occurs in masses of small cubes or square plates. Grape-sugar is also less soluble in water, but more soluble in alcohol, than cane-sugar. Grape-sugar reduces cupric salts and ammonio-nitrate of silver.

According to Fresenius, the percentage proportion of saccharine matter in the dried fig is 60 to 70, grape 10 to 20, cherry 11, mulberry 9, currant 6, whortleberry 6, strawberry 6, raspberry 4 (*Rubus Idæus*, U. S. P.).

Lævulose is lævogyrate, while sucrose and glucose possess right-handed rotation; the latter twist a ray of polarized light from left to right to an extent dependent on the amount of sugar present—a fact easy of application in estimating the amount of sugar in syrups or in diabetic urine.

Cane-sugar, maltose, and grape-sugar yield alcohol and carbonic acid gas by fermentation, the cane-sugar probably always passing into grape-sugar before the production of alcohol commences.

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

In *bread-making* some of the starch is converted into dextrin, and this into sugar by the ferment. The above action then goes on, the liberation of gas producing the *rising* or swelling of the mixture of flour, water, and yeast (dough), the temperature to which the mass is subjected in the oven causing escape of most of the alcohol, and further expansion of the bubbles of carbonic acid gas in every part of the now spongy loaf. The carbonic acid gas gradually evolved when flour is worked up for bread with a mixture of dry bicarbonate of sodium and tartaric acid (best preserved by previous admixture with dried flour and a little carbonate of magnesium, *baking-powder*) exerts similar influence. The least objectionable method of introducing carbonic acid gas, however, is that of Dauglish, whose patent aërated bread is made from flour by mere admixture with carbonic acid water under pressure. On removal from the cylinder the resulting dough expands by the natural elasticity of the imprisoned carbonic acid, and the bake-oven completes the process. The crumb of bread is official in Great Britain (*Mica Panis*, B. P.).

Milk-sugar, or *lactose* ($C_{12}H_{24}O_{12}$) (*Saccharum Lactis*, U. S. P.), the sweet principle of the milk of various animals, is not susceptible of alcoholic or vinous fermentation, but it resembles grape-sugar in reducing an alkaline solution of copper with precipitation of suboxide. It is readily obtained from milk by adding a few drops of acid, stirring, setting aside for the *curds* to separate, filtering, evaporating the *whey* to a small bulk, filtering again if necessary, and allowing to cool and crystallize. It usually occurs in trade "in cylindrical masses two inches in diameter, with a cord or stick in the axis, or in fragments of cakes—grayish-white, crystalline on the surface and in its texture, translucent, hard, scentless, faintly sweet, gritty when chewed." It is soluble in 6 parts of cold and 3 of boiling water; slightly soluble in alcohol; insoluble in ether. Powdered milk-sugar is used in pharmacy as a vehicle for potent solid medicines. Milk-sugar is convertible, by the action of dilute acids, into "galactose" and "lactoglucose;" these may be reunited to form milk-sugar. "Milk-sugar, when sprinkled upon 5 parts of sulphuric acid, should acquire not more than a greenish or reddish, but no brown or blackish-brown, color within one hour (abs. of cane-sugar)."—U. S. P.

Action of Alkali on Sugar.—To a little solution of grape-sugar add solution of potash or soda, or solution of carbonate of potassium, and warm the mixture; the liquid is darkened in color from amber to brown, according to the amount of sugar present.

Tests.—The copper reaction, the fermentation process, and the effect of alkalies form three good tests of the presence of grape-sugar, and, indirectly, of cane-sugar. A piece of merino or other woollen material, previously dipped in a solution of stannic chloride and dried, becomes of a brown or black color when dipped in a solution of glucose and heated to about 300° F. by holding before a fire.

Sugar from Starch.—Boil the starch with a little water and a drop of sulphuric acid as for dextrin, but continue the ebullition for several minutes; on testing a portion of the cooled liquid with iodine and another portion with the heated alkaline solution of a copper salt as described on page 411, it will be found that the starch has nearly all become converted into a sugar—dextrose. Maltose is also formed, at first, but by the continued action of the acid is changed to dextrose. When made on a large scale, a warm (131° F.) mixture of starch and water of the consistence of cream is slowly poured into a boiling solution of one part of sulphuric acid in one hundred of water, the whole boiled for some time, the acid neutralized by chalk, the mixture filtered, the liquid evaporated to a thick syrup and set aside; in a few days it crystallizes to a granular mass resembling honey. In this operation a small quantity of dextrin remains with the glucose, but if the process be conducted under pressure, conversion, according to Manbré, is complete. Sugar made from the starch of rice, maize, etc. is now largely used for table syrups, confectioneries, bee-food, and as a partial substitute for malt in brewing. It is known as *patent sugar*, *saccharine*, dextrin-maltose, etc. In the United States dealers commonly term the thick syrup *glucose*, and the further evaporated, solid product grape-sugar.

The sugar in fresh fruits is mainly cane-sugar, but by the action of the acid, or possibly of a ferment in the juice, it is gradually converted into *inverted sugar*, a variety differing from cane-sugar in being uncrystallizable, and in having an inverted or opposite influence on polarized light, twisting the ray from right to left (lævogyrate, having lævo-rotation, hence sometimes termed *lævulose*). Ripe Hips (*Rosæ Caninæ Fructus*, B. P.) contain 30 per cent. of such sugar, besides gum and acid malates and citrates. Fruit-sugar, as gathered in the form of syrup by bees, is probably a mixture of these two varieties. It is gradually altered to a crystalline or granular mass of grape-sugar, as seen in dried fruits, such as Raisins (*Uvæ*, B. P) and the Prune (*Prunum*, U. S. P.), and in solidified honey (*Mel*, B. P. and U. S. P.). This, the common form of grape-sugar, is dextrogyrate, and hence is sometimes termed *dextrose*, to distinguish it from lævulose. Diluted with twice its weight of water, it yields a liquid having a sp. gr. 1.101 to 1.115. "If 1 part of honey be dissolved in 4 parts of water, a clear solution should result, which should not be rendered more than faintly opalescent by a few drops of test-solution of nitrate of silver (chloride) or of nitrate of barium (sulphate). If a small portion of honey be diluted with 1 volume of water and then gradually mixed with 5 volumes of absolute alcohol, it should not become more than faintly opalescent, and should neither become opaque nor deposit a slimy substance at the bottom and along the sides of the test-tube. When incinerated in small portions at a time in a platinum crucible, it should not leave more than 0.2 per cent. of ash (any larger percentage of ash and failure to respond to the preceding tests indicating the presence of glucose or other foreign admixtures). Water boiled with honey, and allowed to cool, should not be rendered blue or green on the addition of test-solution of iodine (abs. of starch) "—U. S. P. Honey often contains pollen, hairs, spores, the dust and dirt from the flowers, and various flocculent matters which cause it to ferment and yield mannite (Stoddart), alcohol, and acetic acid; hence for use in medicine it (*Mel Despumatum*, U. S. P.) should be clarified by melting and straining, while hot, through flannel previously moistened with warm water. A mixture of clarified honey 80 per cent., acetic acid 10 per cent., and water 10 per cent. is official under the name of *Oxymel* (from ὀξὺς, *oxūs*, acid, and *μέλι*, honey). A similar mixture of honey with acetic acid containing the soluble portions of squill-bulbs (*Scilla*, U. S. P.) is known as Oxymel of Squill (*Oxymel Scillæ*, B. P.). Honey or sugar-cane are the bases of the official *Confections*.

"*Honey Dew*" is a viscid saccharine matter occasionally met with on the leaves of the lime, maple, black alder, rose, and other trees. Sometimes it is sufficiently abundant to dry and fall on the ground, forming a veritable "shower of manna." It is a mixture of cane-sugar, inverted sugar, and dextrin.

Barley-sugar is made by simply heating cane-sugar till it fuses, a change from the crystalline to the uncrystallizable condition occurring. *Treacle* (*Theriaca*, B. P.), *Molasses*, or *Melasses* (from *Mel*, honey), chiefly results from the application of too much heat in evaporating the syrups of the sugar-cane; it is a mixture of cane-sugar with uncrystallizable sugar and coloring-matter. Liquorice-root (*Glycyrrhizæ Radix*, B. P.) contains a considerable quantity of uncrystallizable sugar.

Caramel.—Carefully heat a grain or two of sugar in a test-tube until it blackens; the product is *caramel* or *burnt sugar* (the *Saccharum Ustum* of pharmacy). It is used as a coloring agent for gravies, confectioneries, spirits, and similar materials.

Mannite ($C_6H_{14}O_6$).—Boil manna with alcohol, filter, and set aside; mannite separates in colorless shining crystals or acicular masses to the extent of from 60 to 80 per cent. of the manna.

Manna, U. S. P., is a concrete saccharine exudation from the stem of *Fraxinus ornus* and *F. rotundifolia;* it is obtained by making incisions in the stem of the trees. It occurs in "stalactiform pieces from one to six inches in length and one or two inches in width, uneven, porous and friable, curved on one side, of a yellowish-white color, with a faintly nauseous odor and a sweetish taste." Sp. gr. 0.834. Mannite is also met with in celery, onions, asparagus, certain fungi, and sea-weeds, occurs in the exudations of apple and pear trees, and is produced during the vinous fermentation of sugar.

Mannite is an alcohol, the radical of which is sexivalent $(C_6H_8)^{vi}$-6HO (Wanklyn). It is closely related to the sugars, glucose becoming mannite by action of nascent hydrogen:—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Mannite.}}{C_6H_{14}O_6}.$$

Indeed, glucose itself is probably an alcohol of another radical $(C_6H_6)^{vi}6HO$. Mannite does not undergo vinous fermentation in contact with yeast. It is soluble in 5 times its weight of cold water.

Mucic Acid ($H_2C_6H_8O_8$) and *Saccharic Acid* ($H_2C_6H_8O_8$) are two isomeric bodies formed by the action of dilute nitric acid on certain sugars, gum, mannite, etc.

QUESTIONS AND EXERCISES.

727. How are cane-sugar and grape-sugar analytically distinguished?
728. Describe the methods of extracting and purifying cane-sugar.
729. Mention the chief sources of cane-sugar.
730. Give chemical explanations of the different processes of bread-making.
731. How is milk-sugar obtained, and in what respects does it differ from other sugar?
732. By what process may starch be entirely converted into sugar?
733. What is the difference between fruit-sugar and honey?
734. What is Oxymel?
735. Describe the effect of heat on cane-sugar.
736. Describe the source and character of manna.
737. Give the latest view of the constitution of mannite.
738. Whence are mucic and saccharic acids obtained?

THE GLUCOSIDES.

Source.—The glucosides are certain proximate vegetable principles which, by ebullition with dilute acid or other method of decomposition, take up the elements of water and yield glucose, accompanied by a second substance, which differs in each case according to the body operated on. Several of the glucosides which are of pharmaceutical interest will now be considered. Tannin, or tannic acid, is also a glucoside; it has been described among the acids.

There are indications that glucosides may be regenerated from the bodies into which they are converted by heat.

Note on Nomenclature.—The first syllable of the names of glucosides and neutral principles generally is commonly given in allusion to origin; the last syllable is *in*, which sufficiently distinguishes them as a class.

AMYGDALIN ($C_{20}H_{27}NO_{11},3H_2O$).—This body, obtained by Robiquet and Boutron-Charlard in 1830, was the first discovered glucoside (Liebig and Wöhler, 1837). It is a white crystalline substance existing in the bitter (*Amygdala Amara*, U. S. P.) but not in the sweet almond (*Amygdala Dulcis*, U. S. P.). About 2 per cent. is readily extracted by strong alcohol from the cake left when the fixed oil has been expressed from bitter almonds. From the concentrated alcoholic solution ether precipitates the amgydalin.

Make an emulsion of two or three sweet almonds by bruising and rubbing them with water, and notice that it has no odor of essential oil of bitter almonds: add a grain or two of amygdalin, an odor of essential oil of bitter almonds is at once developed. Bruise two or three bitter almonds and rub with water; the volatile oil is again developed (*Oleum Amygdalæ Amaræ*, U. S. P.). Sp. gr. 1.060 to 1.070.

Bitter Almond-water (*Aqua Amygdalæ Amaræ*, U. S. P.) is made by filtering a mixture of 1 part of the oil with 999 parts of distilled water.

The source of the hydride of benzoyl, or essential oil of bitter almonds, in these reactions is the amygdalin, which. under the influence of *synaptase* or *emulsin*, a nitrogenous casein-like ferment existing in both bitter and sweet almonds, splits up into the essential oil, hydrocyanic acid, and glucose:—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Hydride of}\\\text{benzoyl.}}}{C_7H_5OH} + \underset{\substack{\text{Hydrocy-}\\\text{anic acid.}}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

As each molecule of amygdalin yields one of hydrocyanic acid, a simple calculation shows that 17 grains (mixed with emulsion of sweet almonds) will be required to form one grain of real hydrocyanic acid, a quantity equivalent to 50 minims of the dilute hydrocyanic acid of the British Pharmacopœia. The hydrocyanic acid is probably in chemical combination with the oil.

Test.—The reaction between synaptase and amygdalin is applicable as a test of the presence of one by the addition of the other, even when mixed with much organic matter.

Jacobsen obtains benzaldehyd from benzodichloride (dichloromethylbenzol, $C_6H_5CHCl_2$), one of the dichlorotoluenes, by heating with glacial acetic acid, chloride of zinc, and a little water.

Cherry-Laurel Water (*Aqua Laurocerasi*, B. P., by distillation with water from *Laurocerasi Folia*, B. P.) contains hydrocyanic acid derived from a reaction similar to, indeed probably identical with, that just described, for bitter-almond oil is simultaneously produced. But the proportion of amygdalin or analogous body in cherry-laurel leaves is most variable; hence the strength of the water is highly uncertain. It should contain perhaps two to four parts of hydrocyanic acid in ten thousand.

Prunus Virginiana, U. S. P., the bark of *Prunus serotina* or *Cerasus serotina*, the Wild Black Cherry Bark, also furnishes by distillation an essential oil and hydrocyanic acid; quince-seeds also (*Cydonia vulgaris*). The Wild Black Cherry contains amygdalin.

Caution.—Essential oil of almonds is of course highly poisonous. The purified oil or hydrate of benzoyl is almost innocuous; it is obtained on distilling the crude oil with milk of lime and ferrous chloride, and thoroughly drying the product by shaking with fused chloride of calcium. Sp. gr. 1.043 to 1.049. The so-called "artificial oil of bitter almonds" or nitrobenzol ($C_6H_5(NO_2)$), when taken in quantity, has been known to produce death. The presence of nitrobenzol in oil of bitter almonds is detected by adding a little of the oil to a mixture of zinc and diluted sulphuric acid, shaking well, setting aside for an hour or two, filtering off the clear liquid, and adding a little chlorate of potassium; a violet color (actual mauve) is produced. Or the specimen may be shaken with bisulphide of sodium to fix the essential oil, and then with ether, which dissolves out, and on evaporation will yield the nitrobenzol.

ARBUTIN ($C_{24}H_{32}O_{14},H_2O$) is contained in leaves of *Arctostaphylos uva-ursi* and *Chimaphila umbellata* (*Chimaphila*, U. S. P., or *Pipsissewa*). It is a bitter neutral body occurring in acicular crystals, and resolvable by acids into *hydroquinone* ($C_6H_6O_2$) and glucose, and by gentle oxidation into *quinone* ($C_6H_4O_2$) and formic acid. *Ericolin* ($C_{34}H_{56}O_{21}$) is another bitter glucoside in bearberry leaves.

BRYONIN ($C_{48}H_{80}O_{19}$, Walz).—The colorless, bitter, indistinctly crystalline principle of Bryony (*Bryonia*, U. S. P., the root of *Bryonia alba* and *Bryonia dioica*).

CATHARTIC ACID.—"The glucoside acid that now is known to confer on the Senna of Alexandria (from *Cassia acutifolia*) and of India (from *Cassia elongata*) (*Senna*, U. S. P.) its purgative property has been named by its discoverers (Dragendorff and Kubly) carthartic acid. Its formula has been stated as $C_{180}H_{192}N_4SO_{82}$, which, if true, accounts for its extreme stability. It is insoluble in water, strong alcohol, and ether, but enters readily into watery solution when combined with alkaline and earthy bases, in which state it exists in senna. Its ammonium salts give brownish flocculent precipitates with salts of silver, tin, mercury, copper, and lead.

Antimonial salts, tannin, yellow and red prussiates have no effect upon it. Alkalies, aided by heat, act destructively upon it. Boiled with a mineral acid, it splits into a peculiar kind of glucose and an acid that has been named Cathartogenic; its formula is said to be $C_{132}H_{116}N_4SO_{44}$. The natural cathartate occurring in senna is prepared by partially precipitating by strong spirit a water infusion of senna, concentrated to a syrupy state by evaporation *in vacuo*. The filtrate is now treated with a much larger bulk of absolute alcohol, and the precipitate thus obtained is purified by repeated solution in water and precipitation by alcohol. To obtain the pure acid, advantage is taken of its colloidal properties; the crude cathartate is dissolved in moderately strong hydrochloric acid, and subjected to dialysis on a diaphragm of parchment-paper. The minimum dose of this pure acid was found to be about 1½ grains, which caused several stools with decided griping.

"The cathartic combinations that I have made are the cathartate of ammonium, prepared from cathartate of lead by my original process, and the mixed cathartates, prepared according to Dragendorff's method as modified by myself. Of the former nearly pure salt I have found 3¾ grains to purge fairly as to amount, but slowly as to time, and with considerable griping. Of the latter, 7½ grains purged violently with much griping and sickness, which continued through the greater part of the day. It obviously would be improper to combine senna with any of its metallic precipitants, should such be desired, which is not likely. It is here satisfactory to observe that the cathartate of magnesium is soluble, and that the old-fashioned black draught agrees with new-fashioned science" (Groves).

Buckthorn-juice (*Rhamni Succus*, B. P.) owes its cathartic properties to a substance apparently identical with cathartic acid. Possibly the purgative properties of the bark of the *Rhamnus frangula* (*Frangula*, U. S. P.), *Black alder*, *Buckthorn*, also, are due to cathartic acid.

COLOCYNTHIN ($C_{56}H_{84}O_{23}$?).—This substance is the active bitter and purgative principle of colocynth-fruit (*Colocynthis*, U. S. P.); it is soluble in water and alcohol, but not in ether. By ebullition with acids it furnishes glucose and a resinoid body.

CONVOLVULIN. See JALAPIN.

COTOIN ($C_{22}H_{18}O_6$) appears to be the chief active principle of Coto-bark, a Bolivian remedy for diarrhœa.

DAPHNIN ($C_{31}H_{34}O_{19}$) is the crystalline glucoside of the bark of *Daphne mezereum* (*Mezerei Cortex*, B. P.). Boiled with dilute acids, it yields *daphnetin* ($C_{19}H_{14}O_9$) and glucose. The acrid principle of mezereon is resinoid.

DIGITALIN ($C_{27}H_{45}O_{15}$, Kosman; $C_5H_8O_2$, Schmiedeberg).—This is an active principle of the Foxglove (*Digitalis*, U. S. P.). Boil a grain of digitalin (*Digitalinum*, B. P.) with sulphuric acid for some time; flocks of *digitaliretin* ($C_{15}H_{25}O_5$) separate, and glucose may be detected in the liquid.

$$\underset{\text{Digitalin.}}{C_{27}H_{45}O_{15}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Digitaliretin.}}{C_{15}H_{25}O_5} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Properties.—Digitalin occurs "in porous mammillated masses or small scales, white, inodorous, and intensely bitter, readily soluble in spirit, but almost insoluble in water and in pure ether, dissolves in acids, but does not form with them neutral compounds; its solution in hydrochloric acid is of a faint-yellow color, but rapidly becomes green. It leaves no residue when burned with free access of air. It powerfully irritates the nostrils, and is an active poison." According to Pettenkofer, an intense red color is produced if a trace of digitalin dissolved in water is mixed with a weak aqueous solution of inspissated bile, and sufficient oil of vitriol added to raise the temperature to 158° F. Moistened with sulphuric acid and the liquid exposed to the vapor of bromine, a violet color is produced.

Process.—The process for the preparation of digitalin consists in dissolving the glucoside out of the digitalis-leaf by alcohol, removing the alcohol by distillation, dissolving the residue in water by the help of a small quantity of acetic acid, removing much of the color from the solution by animal charcoal, neutralizing most of the acetic acid by ammonia, precipitating the digitalin by tannic acid (with which it forms an insoluble compound), washing the precipitate, rubbing and heating it with spirit and oxide of lead (which removes the acid in the form of insoluble tannate of lead), again decolorizing by animal charcoal, evaporating to dryness, washing out impurities still remaining by ether, and drying the residual digitalin. In this form digitalin is uncrystallizable.

Pure Digitalin (?)—On treating commercial digitalin with chloroform only an inert substance remains undissolved. The solution yields pure digitalin on evaporation; it may be crystallized from spirit in radiating needles (Nativelle). The therapeutic effect of the pure substance is identical with the preparations of digitalis, but, as might be expected, more constant in its action, and of course intensely powerful. *Digitoxin* ($C_{31}H_{33}O_7$) is a highly poisonous substance extracted from Foxglove by Schmeideberg. The same chemist regards commercial digitalin from Foxglove-seeds as composed of three glucosides—namely, pure *Digitalin* ($C_5H_8O_2$), *Digitonin* ($C_{31}H_{52}O_{17}$), closely allied to saponin, and *Digitalein*.

ELATERIN ($C_{26}H_{28}O_5$).—Boil elaterium, the dried sediment from the juice of the squirting cucumber-fruit (*Ecballium Elaterium*), in a small quantity of spirit of wine, and filter; fibrous and amylaceous matters remain insoluble, while elaterin and resin are dissolved. The filtrate, concentrated and poured into a warm solution of potash, yields, on cooling, crystals of elaterin, resin being retained by the alkali.* It is purified by recrystallization from spirit (*Elaterin*, U. S. P.). Boil elaterium in dilute sulphuric acid for an hour or two, filter, and test the clear liquid for glucose; a reddish precipitate of cuprous oxide falls. This reaction is readily obtained with elaterium, but not always with elaterin; hence probably the latter is not a true glucoside. Walz states that elaterium also contains *prophetin*, a true glucoside.

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* "The alcoholic solution should not be precipitated by tannic acid nor by salts of mercury or of platinum (abs. of, and difference from, alkaloids)."

Elaterin is the active principle of the so-called elaterium. Elaterium occurs "in light, friable, slightly-incurved cakes, about one line ($\frac{1}{12}$ inch) thick, greenish-gray, acrid and bitter; fracture finely granular." Good specimens of this drug should yield, according to the British Pharmacopœia, not less than 20 per cent. of elaterin by the above process. Elaterium adulterated with chalk and other substances was formerly occasionally met with. A Trituration of Elaterin is official (*Trituratio Elaterini*). It is a mixture of 1 part of elaterin with 9 of sugar of milk.

According to the experience of Flückiger and Hanbury, the best method of obtaining elaterin is to exhaust elaterium with chloroform, and then to add ether to the chloroform, when crystalline elaterin is precipitated. It should be washed with a little ether and crystallized from chloroform. When pure it occurs in hexagonal scales or prisms.

Test.—A little is placed in a watch-glass with a drop or two of liquefied carbolic acid, and then two or three drops of strong sulphuric acid; a carmine color is developed (Lindo).

GENTIOPICRIN, or GENTIAN-BITTER ($C_{20}H_{30}O_{12}$), the neutral crystalline principle of the root of *Gentiana lutea* (*Radix Gentianæ*, B. P.). It is soluble in water and weak spirit. Alkalies decompose it. Dilute acids convert it into *gentiogenin* and glucose. Gentian-root also contains a variety of tannin and a crystalline acid ($HC_{14}H_9O_5$) termed *gentianic* or *gentisic acid* or *gentisin.* Fused potash, etc. gives with the latter an acid ($C_7H_6O_4$) which has also unfortunately been called gentisic acid.

GLYCYRRHIZIN ($C_{24}H_{36}O_9$, Gorup-Besanez). — Liquorice-root (*Glycyrrhiza*, U. S. P.) in addition to uncrystallizable sugar contains a sweet substance, *glycyrrhizin*, which, when boiled with hydrochloric acid or dilute sulphuric acid, yields a resinoid bitter body, *glycyrrhetin*, and an uncrystallizable sugar resembling glucose. Glycyrrhizin is only slightly soluble in cold water, but is taken up by diluted alcohol containing a little ammonia (*Extractum Glycyrrhizæ Fluidum*, U. S. P.) or by ammoniacal water. An infusion in the latter, evaporated to a pilular consistence, forms *Extractum Glycyrrhizæ Purum*, U. S.

P. It is present in considerable quantity in the evaporated decoction (*Stick Liquorice*, *Spanish Liquorice*, or *Solazzi Juice*). The tropical substitute for liquorice is the root of *Abrus precatorius*, or *Indian Liquorice* (*Abri Radix*, P. I.), which also apparently contains glucose and glycyrrhizin. Glycyrrhizin has considerable power of disguising nauseous flavors. Roussin refers the sweet taste of liquorice not to pure glycyrrhizin, but to a combination of glycyrrhizin with alkalies, and states that ammoniacal glycyrrhizin has exactly the sweetness of liquorice-root. The formula of this *glycyrrhizate of ammonium* is said by Habermann to be $(NH_4)_3C_{44}H_{60}NO_{18}$. Sestini finds that the glycyrrhizin of liquorice-root is chiefly glycyrrhizate of lime. An Ammoniated Glycyrrhizin (*Glycyrrhizinum Ammoniatum*, U. S. P.) is directed to be prepared by precipitating a dilute ammoniacal percolate with sulphuric acid, washing, redissolving in ammoniacal water, reprecipitating, again washing, dissolving in solution of ammonia, and spreading on glass plates to dry until reddish-brown scales are obtained.

GUAIACIN.—Resin of guaiacum (*Guaiaci Resina*, U. S. P.), an exudation from the wood (*Guaiaci Lignum*, U. S. P.) of *Guaiacum officinale*, is probably a mixture of several substances, among which are *Guaiaretic*, or *Guaiaretinic acid* ($C_{20}H_{26}O_4$) (Hlasiwetz), *Guaiaconic acid* ($C_{38}H_{40}O_{10}$) (Hadelich), and *Guaiacin*, a glucoside. On boiling guaiacum resin with dilute sulphuric acid for some time, glucose is found in the liquid, a green resinous substance (*guaiaretin*) remaining insoluble (Kosmann). Most oxidizing agents, and even atmospheric air, especially under the influence of certain organic substances, produce a blue, then green, and finally a brown color, when brought into contact with an alcoholic solution of guaiacum resin.

These effects are said to be due to three stages of oxidation (Jonas). They may be observed on adding the solution to the inner surface of a paring of a raw potato.

HELLEBORIN ($C_{36}H_{42}O_6$) and HELLEBOREIN ($C_{26}H_{44}O_{15}$) are crystalline glucosides occurring in the roots of Black Hellebore (*Helleborus niger*), or Christmas Rose, and Green Hellebore (*H. viridis*), ranunculaceous herbs.

JALAPIN ($C_{31}H_{50}O_{16}$) AND CONVOLVULIN ($C_{31}H_{56}O_{16}$).—According to Keyser and Meyer, jalap resin contains two distinct substances—convolvulin, chiefly obtained from Mexican male jalap (*Ipomœa orizabensis*), and jalapin, most largely contained in the true jalap (*Ipomœa purga*); the former is soluble in ether, the latter insoluble. Boil jalap resin with dilute sulphuric acid for some time, and filter; a substance, which is probably a mixture of *jalapinol* ($C_{13}H_{24}O_3$) and *convolvulinol* ($C_{16}H_{30}O_3$), separates, and glucose may be detected in the clear liquid. (It is to be regretted that the authors transpose the above names, terming the old well-known jalapin convolvulin.)

$$\underset{\text{Jalapin.}}{C_{31}H_{50}O_{16}} + \underset{\text{Water.}}{5H_2O} = \underset{\text{Jalapinol.}}{C_{13}H_{24}O_3} + \underset{\text{Glucose.}}{3C_6H_{12}O_6}$$

Jalapic Acid.—This is contained in the portion of jalap resin soluble in ether. It may also be obtained from jalapin by ebullition with alkalies:—

$$\underset{\text{Jalapin.}}{2C_{31}H_{50}O_{16}} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Jalapic acid.}}{C_{62}H_{106}O_{35}}$$

Jalap resin (*Resina Jalapæ*, U. S. P.) is obtained by digesting and percolating jalap tubercles (*Jalapa*, U. S. P.) with spirit of wine, distilling off most of the spirit, pouring into water, decanting the aqueous portion, which contains much saccharine matter, and washing and drying the residual resin. The tincture is sometimes decolorized by animal charcoal, and the evaporated product sold as "jalapin."

Jalap resin is insoluble in oil of turpentine; common resin or rosin, soluble. If the presence of the latter is suspected, the specimen should be powdered, digested in turpentine, the mixture filtered, and the filtrate evaporated; no residue, or not more than yielded by the turpentine itself, should be obtained.

Tampico Jalap, from *Ipomœa simulans*, yields a resin, which apparently is chiefly convolvulin, but sometimes contains jalapin; for a sample obtained by Hanbury was entirely soluble in ether, and another extracted by Umney was almost wholly soluble, while Evans purified some, half only of which was soluble.

The *Kaladana resin* or *Pharbitisin* of India (from *Pharbitis Nil*, P. I.) is a cathartic analogous to, if not identical with, resin of jalap.

PICROTOXIN (U. S. P.) is a crystalline bitter poisonous principle (πικρὸς, *picros*, bitter, and τοξικὸν, *toxicon*, poison) occurring in *Cocculus indicus*, the dried fruits of *Anamirta cocculus* (*Anamirta paniculata*, Colebrooke). Ludwig regarded it as a glucoside. Barth and Kretschy state that the so-called picrotoxin may be separated into *picrotoxin* proper ($C_{15}H_{16}O.H_2O$), which is bitter and poisonous; *picrotin* ($C_{25}H_{30}O_{12} + nH_2O$), which is bitter, but not poisonous; and *anamirtin* ($C_{19}H_{24}O_{10}$), which is neither bitter nor poisonous.

SALICIN ($C_{13}H_{18}O_7$).—This substance (*Salicinum*, U. S. P.) is contained in and easily extracted from the bark of the willow, *Salix alba*, and from other species of *Salix* (*Salix*, U. S. P.), especially from *Salix helix*.

Tests.—1. To a small portion of salicin placed on a white plate or dish add a drop of strong sulphuric acid; a deep red color is produced.

2. Boil salicin with dilute sulphuric acid for some time; it is converted into *saligenin* ($C_7H_8O_2$) and glucose.

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + \underset{\text{Water.}}{H_2O} = \underset{\text{Saligenin.}}{C_7H_8O_2} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

Examine a portion of the solution for grape-sugar by the copper-test.

3. To another portion of the liquid, carefully neutralized, add a persalt of iron; a purplish-blue color is sometimes produced, due to the reaction of the saligenin and the ferric salt. The saligenin is, however, so rapidly decomposed by acids into *saliretin* (C_7H_6O) and water that this reaction is almost valueless as a test. Saligenin may readily be obtained by action of synaptase on salicin.

4. Heat a mixture of about 1 part of salicin, 1 of red chromate of potassium, 1½ of sulphuric acid, and 20 of water in a test-tube; a fragrant characteristic odor is evolved, due to the formation of hydride of salicyl ($C_7H_5O_2H$), an essential oil identical with that existing in meadow-sweet (*Spiræa ulmaria*) and in heliotrope.

$$\underset{\text{Saligenin.}}{2C_7H_8O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Hydride of}\\\text{salicyl.}}}{2C_7H_5O_2H} + \underset{\text{Water.}}{2H_2O}$$

Santonin ($C_{15}H_{18}O_3$).—This substance is apparently the anhydride of a weak acid (Hesse), insoluble in ammonia, but forming a soluble calcium salt. Indeed, by boiling santonin for twelve hours with baryta-water, Cannizarro has obtained a salt from which hydrochloric acid separates *santonic acid. Santoninate of Sodium* (*Sodii Santoninas*, U. S. P.) has the formula $2NaC_{15}H_{19}O_4,7H_2O$, and occurs in colorless crystals unstable when exposed to light. From a solution of santonate of calcium the santonin is precipitated by acids. Boiled for some time with dilute sulphuric acid, it yields 87 per cent. of an insoluble resinous substance (*santoniretin*) and glucose (Kosmann). Santonin (*Satoninum*, U. S. P., and *Trochischi Sodii Santoninatis*, U. S. P.) is official. It is soluble in an aqueous solution of twice its weight of carbonate of sodium.

Process.—The process for its preparation consists in boiling *Santonica*, U. S. P. (the unexpanded flower-heads of *Artemisia maritima*, U. S. P., or *Levant Wormseed*), with milk of lime (whereby santonate of calcium is formed), straining, precipitating the santonin or santonic acid by hydrochloric acid or acetic acid, washing with ammonia to remove resin, dissolving in spirit, and digesting with animal charcoal to get rid of coloring-matter, setting the spirituous solution aside to deposit crystals of santonin, and purifying by recrystallization from spirit (Mialhe).

Test.—To highly dilute solution of perchloride of iron add an equal bulk of concentrated sulphuric acid. To this reagent add the santonin, or powder or substance suspected to be santonin, and cautiously apply heat. A red purple, and finally violet, color is produced (Lindo). Santonin added to warm alcoholic solution of potash yields a violet-red color.

Tanacetic acid, from the leaves and tops of *Tanacetum vulgare*, or *Tansy* (*Tanacetum*, U. S. P.), is a yellow crystalline acid having the medicinal properties of santonin.

SAPONIN ($C_{12}H_{20}O_7$?) is a peculiar glucoside occurring in Soapwort, the root of the common Pink, and many other plants; its solution in water, even though very dilute, froths like a solution of soap. Pereira considers *smilacin* (*Salseparin* or *Parallin*), one of the principles of the supposed activity of the root of *Smilax officinalis*, or Sarsaparilla (*Sarzæ Radix*, B. P., *Sarsaparilla*, U. S. P.), to be closely allied to, if not identical with, saponin.

Saponin is also met with in the root of *Polygala senega* (*Senega*, U. S. P.), though the active principle of senega is said to reside in *polygalic acid*, probably a glucosidic derivative of saponin.

According to Klunge (*Pharmacographia*), parallin, by action of acids, yields *parigenin*. The aqueous solutions of parallin froth when shaken.

Saponin is readily obtained from the bark of *Quillaia saponaria*, or *Soap-bark* (*Quillaia*, U. S. P.), by boiling the aqueous extract in alcohol and filtering while hot. Flocks of saponin separate on cooling. It is a white, non-crystalline, friable powder.

SCAMMONIN ($C_{34}H_{56}O_{16}$).—Boil resin of scammony (*Resina Scammonii*, U. S. P.) with dilute sulphuric acid for some time; glucose may then be detected in the liquid, a resinous acid termed *scammoniol* ($C_{14}H_{13}O_3$?) being produced at the same time.

Natural scammony (*Scammonium*, U. S. P.) is an exudation from incisions in the living root of *Convolvulus scammonia*. It contains from 10 to 20 per cent. of gum, and therefore, when rubbed up with water, gives an emulsion. "Ether removes from 80 to 90 per cent. of resin" (B. P.). The official resin of scammony contains no gum, and therefore gives no emulsion when rubbed up with water. It is made by digesting the root in spirit, distilling off the alcohol, and washing the residual resin with water till free from the gum. There seems to be little or no chemical difference between the extracted resin and the resin of the exuded scammony.

Resin of scammony is soluble in all proportions in ether. Spirgatis states that it is identical with the resin of Mexican Male Jalap, which also is soluble in ether. Sulphuric acid slowly reddens it. It is said to be liable to adulteration with resin of true jalap, guaiacum resin, and common rosin. Resin of true jalap is insoluble in ether; guaiacum resin is distinguished by the color-test mentioned under GUAIACIN, and rosin by the action of sulphuric acid.

SCILLITIN.—Schroff, and, afterward, Riche and Remont, believed the bitter principle of the squill-bulb (*Scilla*, U. S. P.) to be a glucoside. Merck has extracted substances which he has termed *scillipicrin* and *scillitoxin*. But no definite crystalline principle has yet been obtained. Schmeideberg has given the name *sinistrin* to a squill principle. Squill contains a large quantity of mucilage.

The bulbous root of *Crinum asiaticum* is official in the Pharmacopœia of India (*Crini Radix*, P. I.) as a substitute for squill. It has not been chemically investigated.

QUESTIONS AND EXERCISES.

739. Define glucosides, and mention those of pharmaceutical interest.

740. Draw out an equation illustrative of the development of Oil of Bitter Almonds.

741. How much pure amygdalin will yield one grain of real hydrocyanic acid?

742. To what does Cherry-Laurel water owe its activity? Is the preparation trustworthy?

743. Mention the active principle of Senna.

744. By what process is the glucoside of the purple foxglove prepared?

745. State the circumstances under which Guaiacum Resin and Jalap Resin yield glucose.

746. Mention a test for guaiacum resin.

747. How may the adulteration of jalap resin by rosin be detected?

748. Enumerate the tests for Salicin.

749. How is santonin officially prepared?

750. Name sources of saponin.

751. What is the difference between Scammony and Resin of Scammony?

752. How would you detect resins of turpentine, guaiacum, or jalap in resin of scammony?

ALCOHOL AND ALLIED BODIES.

ALCOHOL, OR HYDRATE OF ETHYL.

Formation of Alcohol.—Ferment two or three grains of sugar by dissolving in a test-tube full of water, adding a little yeast (*Cerevisiæ Fermentum*, B. P.) or a piece of the so-called German or dried yeast, and set the whole aside for several hours in a warm place at a temperature of 70° or 75°; carbonic acid gas is evolved, and, if the tube be inverted in a small dish containing water, may be collected in the upper part of the tube and subsequently tested: the solution contains alcohol. If the experiment be made on larger quantities (4 ounces of sugar, 1 of yeast, and 1 pint of water) the fermented liquid should be distilled, one-half being collected, shaken with a little lime, soda, or potash, to neutralize any acetic acid and decompose ethereal salts, and again distilled till one-half has passed over; the product is dilute spirit of wine. It may be still further concentrated or *rectified* by repeating this process of *fractional distillation.*

Fermentation.—The act of fermentation is commonly the result, or rather accompaniment, of some vital action. *Alcoholic fermentation* would appear to be always attended by or to attend development of life and free multiplication of cellular structure. It follows the development of the fungus already referred to as constituting the chief active part of yeast, the *Saccharomyces cerevisiæ.* In the presence of this fungus, with small quantities of phosphates and albumenoid matter, *glucose* is converted into alcohol and carbonic acid gas, together with small proportions of glycerin, succinic acid, and other substances. Yeast also contains a soluble ferment analogous to diastase, which is capable of converting sucrose into glucose. Therefore, if yeast be used, *sucrose* or cane-sugar may be converted into carbonic acid gas and alcohol, the soluble ferment first converting the sucrose into glucose.

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{2CO_2}$$

Not more than 20 per cent. by weight of alcohol can be obtained in a fermenting fluid, for more than this proportion prevents fermentation.

Other kinds of fermentation, arising from the action of special ferments which have not received in all cases distinctive names, are the following: *Viscous* or *Mannitic fermentation*, which occurs when beer or saccharine juices, such as that of beet-root, become "ropy." Gum, mannite, and carbonic acid gas are produced. For *Lactic* and *Butyric fermentations* see Lactic Acid. *Putrefactive fermentation* occurs when a liquid containing albumenoid matter is exposed to the air. Infusoria appear in the liquid, using up the dissolved oxygen, and the ferments of the genus *Vibrio* are developed. These are protected from oxygen, which is fatal to them, by a thin surface-layer crowded with bacteria—small rod-like organisms having powers of locomotion. The vibrionic action, or putrefaction, proceeds with evolution of sulphuretted hydrogen, together with other gases having unpleasant odors and of complex chemical constitution. For *Acetic fermentation* see Acetic Acid. For *Ammoniacal fermentation*, see Urine.

Fermentation by Certain Soluble Albumenoids.—For the conversion of starch into sugar by diastase, see Starch; of amygdalin into benzoic aldehyd, hydrocyanic acid, and glucose by emulsin, see Amygdalin; of salicin into saligenin and glucose, see Salicin; of myronate of potassium into sulphocyanide of allyl, etc. by myrosin, see Mustard; of cane-sugar into grape-sugar by the soluble ferment in yeast, see the foregoing paragraphs.

Alcoholic Fermentation.—The chief reaction results, as already stated, in the formation of alcohol and carbonic acid gas, though traces of several other substances are simultaneously produced (*vide*

"Fusel Oil" in Index). By this reaction are formed the spirit of the various kinds of wine, beer, and liqueurs: Sherry Wine (*Vinum Xericum*, B. P.) and Port Wine, the fermented juice of the grape; Whiskey (*Spiritus Frumenti*, U. S. P.), containing from 48 to 56 per cent. of pure alcohol; *Spirit of Myrcia*, or *Bay Rum* (*Spiritus Myrciæ*, U. S. P.), prepared by dissolving the oils of *Myrcia acris*, pimento, and orange-peel in diluted alcohol; and others.

Alcoholic drinks vary much in strength. Cider or apple wine, cherry or pear wine, and good beer (ale and porter, or stout) contain 4 to 6 per cent. of real alcohol; good light wines, both "red" and "white," 10 to 12 per cent.; good sherry and port, which are commonly "fortified"—that is, contain added spirit—16 or 18 per cent.; while "spirits" (gin, rum, brandy, whiskey, etc.) and "liqueurs" (ratafia, almond-flavored; maraschino, cherry-flavored; curaçoa, orange-flavored; chartreuse, a composite-flavored liqueur, etc.) are "under proof" or "over proof," terms explained in the next paragraph. The well-known effects of these fluids on the animal system would appear to be due primarily to alcohol, and, secondarily, to ethereal derivatives of alcohols. Some owe a part of their effects to non-volatile substances, for beer, from which all alcohol has been removed by ebullition, still has a powerful influence on the human economy. The official (U. S. P.) Wines are all made with "Stronger White Wine" (*Vinum Album Fortius*, U. S. P.), made by adding 1 part of alcohol to 7 parts of "White Wine" (*Vinum Album*, U. S. P.), the latter a kind of natural sherry containing not less than 10 nor more than 12 per cent. of absolute alcohol. *Vinum Rubrum*, U. S. P., is of similar strength—a kind of natural port wine.

Varieties of Alcohol.—The weak spirit concentrated by distillation till it contains 84 per cent. by weight of pure alcohol is an ordinary article of British trade; its specific gravity at 60° F. is 0.8382. This is common *Spirit of Wine*, the *Spiritus Rectificatus* of the British Pharmacopœia. The British official *Proof Spirit** (*Spiritus Tenuior*, B. P.) contains 49 per cent. by weight of alcohol, and is made by diluting 100 volumes of Rectified Spirit with water until the well-stirred product measures 156 volumes. Sixty volumes of water will be required for this purpose, the liquids occupying less bulk after than before admixture. In the language of the Excise authorities, the rectified spirit of the Pharmacopœia would be described as "56 per cent. over proof" (56 per cent. O. P.); that is, 100 volumes contain as much alcohol as is present in 156 volumes of proof spirit. Obviously, proof spirit may be made by diluting with water rectified spirit of any other strength than that mentioned above. Thus 100 fluidounces of a spirit of "seventy over proof" may be diluted to 170, or the same quantity of a spirit of "fifty over proof" may be diluted to 150, and so on. The specific gravity of proof spirit at 60° is 0.920.

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* *Proof spirit* is so termed from the fact that in olden times a proof of its strength was supposed to be afforded by moistening a small quantity of gunpowder and setting light to the spirit; if it fired the powder, it was said to be "over proof;" if not, "under proof." The weakest spirit that would stand this test was what we should now describe as of sp. gr. 0.920.

Alcohol, U. S. P., contains 91 per cent. by weight (94 by volume), *Alcohol Dilutum*, U. S. P., 45½ per cent. by weight (53 by volume) of real alcohol, the remainder being water. The former has a sp. gr. of 0.820, the latter 0.928, at 15.6° C., or 0.812 and 0.920, respectively, at 25° C. The stronger boils at 78° C.

Empirical Formulæ—Composition of Alcohol.—Alcohol by quantitative analysis is found to contain the elements carbon, hydrogen, and oxygen in the following proportions:—

Composition of Alcohol.

Carbon . . .	52.174,	or ÷ 12 = 4.348, or 2.
Hydrogen . . .	13.043,	or ÷ 1 = 13.043, or 6.
Oxygen . . .	34.783,	or ÷ 16 = 2.174, or 1.
	100.000	

From centesimal numbers a formula is obtained in the usual way. Thus, on dividing these figures by the atomic weights of the respective elements ($C = 12$, $H = 1$, $O = 16$), and reducing the products to the simplest whole numbers, alcohol will be found to contain two atomic weights of carbon to every six of hydrogen and to every one of oxygen, and its possible or *empirical formula* to be C_2H_6O.

Constitution of Alcohol.—There is good reason to believe that alcohol is the hydrate of a basylous radical *ethyl* (C_2H_5 or Et); hence we derive the *rational formula* C_2H_5HO or EtHO. Sodium displaces hydrogen from alcohol, *ethylate of sodium*, or "caustic alcohol," being produced: $Na_2 + 2EtHO = H_2 + 2EtNaO$.

Rational Formulæ.—Rational formulæ are deduced by (1) ascertaining how much of the substance will combine with, displace, or play the part of, the atomic weight of a well-known element or radical. When this method cannot be applied, or in confirmation of it, processes of (2) reduction, (3) oxidation, (4) substitution, etc. are employed.

Salts of Ethyl.—Alcohol is, then, a body analogous in constitution to hydrate of potassium (KHO); and there are other compounds of ethyl analogous in constitution to ordinary inorganic salts, such as those of potassium. The oxide of ethyl (Et_2O) is common ether; the nitrite of ethyl ($EtNO_2$) is the chief body which, dissolved in spirit of wine, constitutes "sweet spirit of nitre;" the acid sulphate of ethyl ($EtHSO_4$), or sulphethylic or sulphovinic acid, is a liquid met with in the preparation of ether. The iodide (EtI), hydride (EtH), acetate ($Et\bar{A}$), and other salts are of considerable chemical interest, but not used in medicine.

Absolute or Real Alcohol (C_2H_5HO) may be prepared from spirit of wine by removing the water which the latter contains. This is accomplished, partially, by anhydrous carbonate of potassium, and finally and entirely by recently-burned quicklime. In operating on, say, one pint, 1½ ounces of dried carbonate of potassium are placed in a bottle that can be well closed, and frequently shaken during two days with the spirit. Meanwhile, about half a pound of good quicklime, if not already at hand, is made from 10 or 11 ounces of slaked lime by heating to redness in a covered crucible for half an hour. The spirit having been decanted from the denser aqueous solution of carbonate of potassium and placed in a quart flask, retort, or tin can, the lime, as soon as cold, is added, and the whole occasionally shaken during a day. The vessel is now placed in a saucepan or other bath containing water, quickly connected with a condenser (in the case of the flask or can by a bent tube and cork previously prepared, for absolute alcohol must not be exposed to air, or water in the form of moisture will be rapidly reabsorbed), and heat applied to the bath. Rejecting the first ounce or ounce and a half, as likely to contain traces of moisture absorbed from the air or apparatus, continue distillation until nothing more passes over, the water in the bath being kept just below the boiling-point (about 200° F.). These details are those of the British Pharmacopœia. Specific gravity 0.7938; boiling-point, 173° F.

Tests.—There are no specific tests for alcohol when mixed with complex matters. It is, however, easily isolated and concentrated by fractional distillation, and is then recognizable by conjoint physical and chemical characters. Thus its odor and taste are characteristic; it is lighter than water, volatile, colorless, and, when tolerably strong, inflammable, burning with an almost non-luminous flame; it readily yields aldehyd (see below) and acetic ether (*vide* p. 436), each of which has a characteristic odor; lastly, in presence of hot acid, alcohol reduces red chromate of potassium to a green salt of chromium.

According to Lieben, 1 of alcohol in 2000 of water can be detected by adding to some of the warmed liquid a little iodine, a few drops of solution of soda, again warming gently, and setting aside for a time; a yellowish crystalline deposit of *iodoform* (CHI_3) is obtained. Under the microscope the latter presents the appearance of hexagonal plates or six-rayed and other varieties of stellate crystals.

$$C_2H_6O + 4I_2 + 6NaHO = CHI_3 + NaCHO_2 + 5NaI + 5H_2O.$$

Other alcohols, aldehyds, gum, turpentine, sugar, and several other substances give a similar reaction.

Tests of Purity.—Oil or resin is precipitated on diluting spirit of wine with distilled water, giving an opalescent appearance to the mixture. The specific gravity should be 0.838. Fusel oil, aldehyd, and such impurities are detected by nitrate of silver (*vide* Index, "Alcohol, Test for Purity of"). Water in absolute alcohol may be detected by adding to a small quantity a little highly dried sulphate of copper, which becomes blue ($CuSO_4,5H_2O$) if water is present, but retains its yellowish-white anhydrous character ($CuSO_4$) if water be absent. In the United States Pharmacopœia it is laid down that alcohol, "if mixed with its own volume of water and one fifth its volume of glycerin, a piece of blotting-paper, on being wet with the mixture after the vapor of alcohol has wholly disappeared, should give no irritating or foreign odor (fusel oil). And if a portion be evaporated to one-fifth its volume, the residue should not turn reddish upon the addition of an equal volume of sulphuric acid (amyl alcohol). When treated in a test-tube with an equal volume of solution of potassa, there should not be an immediate darkening of the liquid (methyl alcohol, aldehyd, and oak tannin). If a portion of about 150 c.c. be digested for an hour with 20 gm. of carbonate of lead, and filtered, the filtrate then distilled from a water-bath, and the first 20 c.c. of the distillate treated with 1 c.c. of test-solution of permanganate of potassium, the color should not disappear within one or two minutes (abs. of methyl alcohol)."

ALDEHYD (C_2H_4O).—Place together, in a capacious test-tube, or a flask, about four parts of spirit of wine, six of black oxide of manganese, six of sulphuric acid, and four of water, and gently warm the mixture; aldehyd (*al*cohol *dehyd*rogenatus), a highly volatile liquid, is immediately formed, and its vapor evolved, recognized by its peculiar, somewhat fragrant odor. Adapt a cork and rather long bent tube to the test-tube, and let some of the aldehyd slowly distil over into another test-tube, the condensing-tube being kept as cool as possible. Set the distillate aside for a day or two; the aldehyd will have nearly all disappeared, and acetic acid be found in the tube. Test the exposed liquid by litmus-paper; it will be found to have an acid reaction: make it slightly alkaline by a drop or two of solution of carbonate of sodium, then boil to remove any alcohol and aldehyd present, add sulphuric acid, and notice the characteristic odor of the acetic acid evolved.

These experiments will enable the process of acetification described in connection with acetic acid to be more fully understood. Pure diluted alcohol is not oxidized by exposure to air; but in presence of fermentive matter, or vegetable matter undergoing decay or change, it is oxidized first to aldehyd and then to acetic acid.

In the above process the black oxide of manganese and sulphuric acid furnish nascent oxygen:—

$$\underset{\substack{\text{Black oxide}\\\text{of manganese.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate of}\\\text{manganese.}}}{MnSO_4} + \underset{\substack{\text{Oxygen}\\\text{(atom).}}}{O} + \underset{\text{Water.}}{H_2O}.$$

The nascent oxygen then acts on the alcohol, just as the oxygen of the air acts on the alcohol in fermented infusion of malt, beer, or wine, giving aldehyd:—

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\substack{\text{Oxygen}\\\text{(atom).}}}{O} = \underset{\text{Aldehyd.}}{C_2H_4O} + \underset{\text{Water.}}{H_2O}$$

The aldehyd rapidly, even when pure (more rapidly when impure), absorbs oxygen and yields acetic acid:—

$$\underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{2C_2H_4O_2}$$

Tests.—Aldehyd heated with solution of potash gives a brownish-yellow resinous mass of peculiar odor. Its aqueous solution reduces salts of silver, giving a mirror-like coating to the sides of a test-tube.

Spirit of French Wine (*Spiritus Vini Gallici*, U. S. P.), or *Brandy*, is a colored and flavored variety of alcohol distilled from French wine. Its color is that of light sherry, and is derived from the cask in which it has been kept, but it is commonly deepened by the addition of burnt sugar. Its taste is due to the volatile flavoring constituent of the wine, often increased by the addition of artificial essences. "Brandy has a pale amber color, a distinctive taste and odor, and a sp. gr. not above 0.941 nor below 0.925, corresponding approximately with an alcoholic strength of 39 to 47 per cent. by weight, or 46 to 55 per cent. by volume. If 100 c.c. of brandy be slowly evaporated in a weighed capsule, on a water-bath, the last portions volatilized should have an agreeable odor, free from harshness (abs. of fusel oil from grain or potato spirit). The residue, dried at 100° C. (212° F.), should weigh not more than 0.250 gm., equivalent to 0.25 per cent. (abs. of an undue amount of solids). This residue should have no sweet or distinctly spicy taste (abs. of added sugar, glycerin, or spices). It should nearly all dissolve in 10 c.c. of cold water, forming a solution which is colored light green by a dilute solution of ferric chloride (traces of oak tannin from casks). 100 c.c. of brandy should be rendered distinctly alkaline to litmus by 3 c.c. of the volumetric solution of soda (abs. of an undue amount of free acid)."—U. S. P.

The foregoing words are also used in describing *Whiskey* (*Spiritus Frumenti*) in the United States Pharmacopœia, except that the sp. gr. is to be "not above 0.930 nor below 0.917, corresponding approximately with an alcoholic strength of 44 to 50 per cent. by weight, or 50 to 58 per cent. by volume," and that the acidity is not to be greater in 100 c.c. than 2 c.c. of soda solution will neutralize.

QUESTIONS AND EXERCISES.

753. Write a few sentences on the formation, purification, and concentration of alcohol, and explain the difference between Rectified Spirit, Proof Spirit, and Absolute Alcohol.

754. What quantity of water must be added to one gallon of spirit of wine, 56 degrees over proof, to convert it into proof spirit?

755. To what volume must 5 pints of spirit of wine of 53 degrees over proof be diluted before it becomes proof spirit? *Ans.* 7 pints, 13 ounces.

756. State the specific gravity of proof spirit.

757. Show how the formula of alcohol is obtained from its centesimal composition:—

Carbon	52.174
Hydrogen	13.043
Oxygen	34.783
	100.000

758. Give the formulæ of some of the salts of ethyl.

759. By what processes may pure hydrate of ethyl be obtained?

760. Enumerate the characters of alcohol.

761. Mention a chemical test to distinguish rectified spirit from absolute alcohol.

762. From the formula of aldehyd calculate back its composition in 100 parts.

763. What is the relation of aldehyd to alcohol and to acetic acid?

764. Whence is brandy obtained, and to what are due its color and flavor?

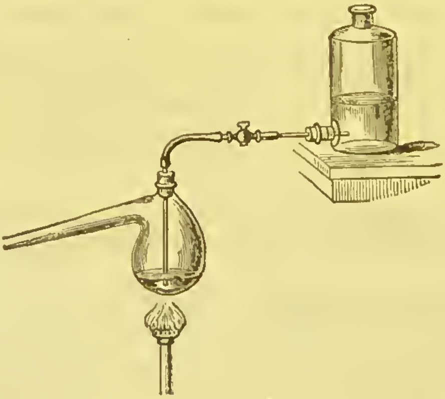
ETHER, OR OXIDE OF ETHYL.

Formula $C_4H_{10}O$, or $(C_2H_5)_2O$, or Et_2O.

Experimental Process.—Into a capacious test-tube put a small quantity of spirit of wine and about half its bulk of sulphuric acid, mix and gently warm; the vapor of ether, recognized by its odor, is evolved. Adapt a cork and long bent tube to the test-tube, and slowly distil over the ether into another test-tube. Half the original quantity of alcohol now placed in the generating-tube will again give ether; and this operation may be repeated many times.

On the larger scale, and according to the following process, the addition of alcohol, instead of being intermitting, is continuous, a tube conveying alcohol from a reservoir into the generating-vessel. Mix 10 fluidounces of sulphuric acid with 12 fluidounces of rectified spirit in a glass retort or flask capable of containing at least two pints, and, not allowing the mixture to cool, connect the retort or flask by means of a bent glass tube with a Liebig's condenser, and distil with a heat sufficient to maintain the liquid in brisk ebullition. If a thermometer also be inserted in the tubulure of the

Fig. 49.



retort or through the cork of the flask, the temperature may be still more carefully regulated—between 284° and 290° F. As soon as the ethereal fluid begins to pass over, supply fresh spirit in a continuous stream, and in such quantity as to about equal the volume of the fluid which distils. For this purpose use a tube furnished with a stopcock to regulate the supply, connecting one end of the tube with a vessel containing the spirit supported above the level of the retort or flask, and passing the other end through the cork of the flask into the liquid. When a total of 50 fluidounces of spirit has been added, and 42 fluidounces of ether have distilled over, the process may be stopped.

To *partially purify* the liquid, dissolve 10 ounces of chloride of calcium in 13 ounces of water, add half an ounce of lime, and agitate the mixture in a bottle with the impure ether. Leave the mixture at rest for ten minutes, pour off the light supernatant fluid, and distil it with a gentle heat until a glass bead of specific gravity 0.735 placed in the receiver begins to float. The ether and spirit retained by the chloride of calcium and by the residue of each rectification may be recovered by distillation and used in a subsequent operation.

Explanation of Process.—On the addition of sulphuric acid to alcohol in equal volumes, one molecule of each reacts and gives a molecule of sulphethylic acid and one of water:—

$$\underset{\text{Alcohol.}}{\mathrm{EtHO}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathrm{H_2SO_4}} = \underset{\substack{\text{Sulphethylic}\\ \text{acid.}}}{\mathrm{EtHSO_4}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

More alcohol then gives ether and sulphuric acid by the reaction of one molecule of the alcohol on one of sulphethylic (ethylsulphuric) acid:—

$$\underset{\text{Alcohol.}}{\mathrm{EtHO}} + \underset{\substack{\text{Sulphethylic}\\ \text{acid.}}}{\mathrm{EtHSO_4}} = \underset{\text{Ether.}}{\mathrm{Et_2O}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathrm{H_2SO_4}}$$

The water of the first reaction and the ether of the second distil over, while the sulphuric acid, as fast as liberated, is attacked by alcohol and reconverted into sulphethylic acid:—

$$\underset{\text{Alcohol.}}{\mathrm{EtHO}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathrm{H_2SO_4}} = \underset{\substack{\text{Sulphethylic}\\ \text{acid.}}}{\mathrm{EtHSO_4}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

so that the sulphuric acid originally employed finally remains in the retort in the form of sulphethylic acid. The effect, however, of a small quantity of sulphuric acid in thus converting a large quantity of alcohol into ether is limited, secondary reactions occurring to some extent after a time.

Properties.—Pure ether is gaseous at temperatures above 95° F.; hence the condensing-tubes employed in its distillation must be kept as cool as possible. At all ordinary temperatures it rapidly evaporates, absorbing much heat from the surface on which it is placed. A few drops evaporated consecutively from the back of the hand produce great cold; if blown in the form of spray, the cooling effect is so rapid and intense as to produce local anæsthesia. Its vapor is very heavy, more than twice and a half that of air and nearly forty times that of hydrogen ($H_2 = 2$; $C_4H_{10}O = 74$; or as 1 to 37). In a still atmosphere, therefore, it will flow a considerable distance along a table or floor before complete diffusion occurs; the vapor is also highly inflammable; hence the importance of keeping candle and other flames at a distance during manipulations with ether.

Purification.—To imitate the process of partial purification above described, add to the small quantity of ether obtained in the foregoing operation a strong solution of chloride of calcium and a little slaked lime; the latter absorbs any sulphurous acid that may have been produced by secondary decompositions, while the former absorbs water; on shaking the mixture and then setting aside for a minute or two, the ether will be found floating on the surface of the solution of chloride of calcium.

This ether, redistilled until the distillate has a sp. gr. not higher than 0.735 and boiling-point not higher than 105° F., is the ether of the British Pharmaeopœia. It still contains about 8 per cent. of alcohol. The latter may be removed by well shaking the ether with half of its bulk of water, setting aside, separating the floating ether, and again shaking it with water; alcohol is thus washed out. This washed ether, containing water (for water and ether are to some extent soluble the one in the other; 50 measures agitated with an equal volume of water are reduced to 45 by an absorption of 10 per cent.), is next placed in a retort with solid chloride of calcium and a little caustic lime, and once more distilled; pure dry ether results. Sp. gr. not exceeding 0.720. *Æther*, U. S. P., contains nearly 74 per cent. of real ether, nearly 26 per cent. of alcohol, and a little water; sp. gr. 0.750 at 15° C. *Æther Fortior*, U. S. P., contains nearly 94 per cent. of real ether, nearly 6 per cent. of alcohol, and a little water; sp. gr. not above 0.725 at 15° C., or 0.716 at 25° C.; boiling-point, 37° C. Agitated with an equal volume of glycerin, the *Æther* should yield 75 per cent. of ether, while *Æther Fortior* should yield 86 per cent.

Spiritus Ætheris, U. S. P., is a mixture of 30 weights of ether with 70 similar weights of alcohol. *Spiritus Ætheris Compositus*, U. S. P., contains 30 of stronger ether, 67 of alcohol, and 3 of ethereal oil. It is the old "Hoffmann's Anodyne."

NITROUS ETHER, OR NITRITE OF ETHYL.

Formula $C_2H_5NO_2$ or $EtNO_2$.

Process.—To a third of a test-tubeful of alcohol add about a tenth of its bulk of sulphuric acid, rather more of nitric acid, and warm the mixture as soon as ebullition commences; the vapor of nitrous ether (with other substances) is evolved, recognized by its odor. A long bent tube, kept cool, may be adapted by a perforated cork to the test-tube, and thus a little of the product be condensed and collected.

The above process conducted on a larger scale, with definite quantities of materials, temperature regulated by a thermometer, and a well-cooled condenser, etc. (see p. 125), is the official process for the preparation of a solution of crude nitrous ether. Diluted with spirit, one variety of it forms the "sweet spirit of nitre" (*Spiritus Ætheris Nitrosi*, U. S. P.) of pharmacy, "containing 5 per cent. of the crude ether."

"Add 7 parts of sulphuric acid gradually to 31 parts of alcohol. When the mixture has cooled, transfer it to a tubulated retort connected with a well-cooled condenser, to which a receiver, surrounded by broken ice, is connected air-tight, and which is further connected, by means of a glass tube, with a small vial containing water, the end of the tube dipping into the latter. Now add 9 parts of nitric acid to the contents of the retort, and, having introduced a thermometer through the tubulure, heat rapidly, by means of a water-bath, until strong reaction occurs and the temperatnre reaches 80° C. (176° F.). Continue the distillation at that temperature, and not exceeding 82° C. (180° F.), until the reaction ceases. Disconnect the receiver, and immediately pour the distillate into a flask containing 16 parts of ice-cold distilled water. Close the flask and agitate the contents repeatedly, keeping down the temperature by immersing the flask occasionally in ice-water. Then separate the ethereal layer and mix it immediately with 19 times its weight of alcohol. Keep the product in small, glass-stoppered vials, in a dark place, remote from lights or fire."

"*Properties.*—A clear, mobile, volatile, and inflammable liquid, of a pale straw-color, inclining slightly to green, a fragrant, ethereal odor, free from pungency, and a sharp, burning taste. Sp. gr. 0.823 to 0.825. It slightly reddens litmus-paper, but should not effervesce when a crystal of bicarbonate of potassium is dropped into it. When mixed with half its volume of solution of potassa, previously diluted with an equal volume of water, it assumes a yellow color, which slightly deepens, without becoming brown, in twelve hours. A portion of the spirit, in a test-tube half filled with it, plunged into water heated to 63° C. (145.4° F.), and held there until it has acquired that temperature, should boil distinctly on the addition of a few small pieces of glass.

"*Test.*—If 10 gm. of spirit of nitrous ether be macerated with 1.5 gm. of potassa for twelve hours, with occasional agitation, the mixture then diluted in a beaker with an equal volume of water, and set aside until the odor of alcohol has disappeared, then slightly acidulated with diluted sulphuric acid, and a solution of 0.335 gm. of permanganate of potassium gradually added, the color of the whole of this solution should be discharged (presence of at least 4 per cent. of real ethyl nitrite)."

The nitrous radical may be detected by adding sulphate of iron and sulphuric acid to some of the spirit of nitrous ether, a brown or black compound being produced, already explained in connection with nitric acid (p. 286).

The chief reactions in the above process consist in the reduction of the nitric radical (NO_3) to the nitrous (NO_2) by some of the hot spirit, and the combination of the nitrous radical with the ethyl of more of the spirit.

Acetic Ether, or Acetate of Ethyl.

To a little dried acetate of sodium, in a test-tube, add a small quantity of rectified spirit of wine and some sulphuric acid, and, adapting a long bent tube in the usual manner, heat the test-tube, and so distil over acetic ether, which may be collected in another test-tube kept cool by partial immersion in cold water.

The official proportions (*Æther Aceticus*, B. P.) are 8 parts of dried acetate of sodium, 5 of spirit, and 10 of acid. It is purified from any water by shaking in a bottle with fused chloride of calcium, and, after twenty-four hours, rectifying. "Sp. gr. 0.910. Boiling-point 166° F."

$$\underset{\substack{\text{Hydrate of}\\ \text{ethyl.}}}{C_2H_5HO} + \underset{\substack{\text{Acetate of}\\ \text{sodium.}}}{NaC_2H_3O_2} + \underset{\substack{\text{Sulphate of}\\ \text{hydrogen.}}}{H_2SO_4} = \underset{\substack{\text{Acetate of}\\ \text{ethyl.}}}{C_2H_5C_2H_3O_2} + \underset{\substack{\text{Sulphate of sodium}\\ \text{and hydrogen.}}}{NaHSO_4} + \underset{\text{Water.}}{H_2O}$$

The *Æther Aceticus*, U. S. P., has a sp. gr. of 0.889 to 0.897; boiling-point 76° C. (168.8° F.). When 10 c.c. are agitated with an equal volume of water, in a graduated test-tube, the upper, ethereal layer, after its separation, should not measure less than 9 c.c.

Iodide of Ethyl (EtI) may be prepared by mixing two or three parts of phosphorus with 100 of *absolute* alcohol, and then dropping in iodine gradually until about 200 parts have been added.

$$\underset{\text{Alcohol.}}{5EtHO} + \underset{\substack{\text{Iodide of}\\ \text{phosphorus.}}}{PI_5} = \underset{\substack{\text{Iodide of}\\ \text{ethyl.}}}{5EtI} + \underset{\substack{\text{Phosphoric}\\ \text{acid.}}}{H_3PO_4} + \underset{\text{Water.}}{H_2O}$$

The reaction at first proceeds rapidly, and is complete after the mixture has been set aside for a few hours. The iodide of ethyl may then be isolated by careful distillation, freed from any excess of iodine by washing with a very small quantity of solution of potash or soda, washed with water, dried over chloride of calcium, and again distilled. It should be kept in a dark place, as light favors decomposition and liberation of iodine.

Bromide of ethyl (C_2H_5Br), or *hydrobromic ether*, may be similarly prepared. For its preparation on a large scale De Vrij's method is preferable, $EtHSO_4 + KBr = EtBr + KHSO_4$ (*see Pharm. Journ.*, Feb. 15, 1879), or the same method as modified by Greene (*P. J.*, July 12, 1879); by

Remington (*P. J.*, May 29, 1880); or by Wolff (*P. J.*, July 3, 1880).

ETHYL.—This gaseous radical, $(C_2H_5)_2$ or Et_2, is obtained on digesting together, at about 250° F., in a strong sealed tube, dry, freshly granulated zinc with iodide of ethyl (Frankland).

Zn	+	$2EtI$	=	ZnI_2	+	Et_2
Zinc.		Iodide of ethyl.		Iodide of zinc.		Ethyl.

On cautiously opening the tube the ethyl escapes, and may be ignited or collected over water. There remains with the iodide of zinc a body termed by Frankland *zinc-ethyl* ($ZnEt_2$); it is a spontaneously inflammable liquid, but may easily be distilled and otherwise manipulated if a few simple precautions be observed. If water be allowed to flow down the tube, the solid compound of iodide of zinc and zinc-ethyl will be decomposed, a gas, *hydride of ethyl* (EtH), resulting, which also may be inflamed or collected over water:—

$$ZnEt_2 + 2H_2O = Zn2HO + 2EtH.$$

QUESTIONS AND EXERCISES.

765. Describe the official process for the preparation of Ether, giving equations.

766. Offer a physical explanation of the mode of producing local anæsthesia.

767. How is commercial ether purified?

768. Explain the official process for the preparation of Spirit of Nitrous Ether.

769. Give the properties of spirit of nitrous ether.

770. By what official method is the strength of Spirit of Nitrous Ether estimated?

771. How is iodide of ethyl made?

772. Adduce evidence of the existence of ethyl.

OTHER ALCOHOL RADICALS AND THEIR SALTS.

What has been stated concerning the chemistry of ethyl and its compounds may be applied to other radicals known to exist, some of the compounds of each of which are of common occurrence. These basylous radicals are closely related to each other, to hydrogen, and to the metals. Their formulæ in the combined state may be built up by successive additions of CH_2, thus:—

Hydrogen	H
Methyl	CH_3, or Me
Ethyl	C_2H_5, or Et
Propyl (or Trityl)	C_3H_7, or Pr
Butyl (or Tetryl)	C_4H_9, or Bu
Amyl	C_5H_{11}, or Ay
Caproyl (or Hexyl)	C_6H_{13}, or Cp

The above list is an illustration of an *homologous* series (from ὁμὸς, *homos*, the same, and λόγος, *logos*, proportion) of compounds. It will be observed that the relation of the number of hydrogen atoms to carbon is twice as many, with one added; hence the series is often termed the $C_nH_{2n}+_1$ series (n = any number). The oxides of these radicals are known as *ethers*, their hydrates *alcohols*, their compounds with the acetic and similar acidulous radicals *ethereal salts*. Every alcohol furnishes a body corresponding to the aldehyd of spirit of wine, the class being termed *aldehyds;* each also yields an acid corresponding with acetic acid. Any one of these classes constitutes an homologous series. Or, taking the hydride, oxide, hydrate, acid, of any single radical, we get a *heterologous* (ἕτερος, *heteros*, another) series of compounds. Hydride of methyl (MeH or CH_3H) is ordinary *marsh-gas*, *fire-damp* or *light carburetted hydrogen;* it is a diluent or non-luminiferous constituent of ordinary coal-gas to the extent of 30 or 40 per cent.;* *formic acid*, the acid of the methyl series; *butyric acid*, the acid of the butyl series; *sulphocyanate of butyl*, the essential oil of horseradish; *valerianic acid*, the acid of the amyl series.

Homologous and Heterologous Series of the $C_nH_{2n}+_1$ Radicals.

Radicals (free).	Hydrides.	Oxides (or ethers).	Hydrates (or alcohols).	Aldehyds.	Acids.
$(CH_3)_2$	CH_3H	$(CH_3)_2O$	CH_3HO	CH_2O ?	CH_2O_2
$(C_2H_5)_2$	C_2H_5H	$(C_2H_5)_2O$	C_2H_5HO	C_2H_4O	$C_2H_4O_2$
$(C_3H_7)_2$	C_3H_7H	$(C_3H_7)_2O$	C_3H_7HO	C_3H_6O	$C_3H_6O_2$
$(C_4H_9)_2$	C_4H_9H	$(C_4H_9)_2O$	C_4H_9HO	C_4H_8O	$C_4H_8O_2$
$(C_5H_{11})_2$	$C_5H_{11}H$	$(C_5H_{11})_2O$	$C_5H_{11}HO$	$C_5H_{10}O$	$C_5H_{10}O_2$
etc.	etc.	etc.	etc.	etc.	etc.

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* *Coal-gas.*—The other diluents, or vehicles for the conveyance of illuminating vapors of coal-gas, are hydrogen (40 to 50 per cent.) and carbonic oxide (6 to 7 per cent.). The illuminating constituents are olefiant gas (p. 453) and its homologues, existing to the extent of from 5 to 7 per cent. Hydrocarbons normally fluid, but kept in the vaporous condition by the diluents, also contribute materially to the illuminating power of gas. The impurities are nitrogen, air, carbonic acid, bisulphide of carbon, and badly-smelling sulphur compounds.

QUESTIONS AND EXERCISES.

773. Mention several radicals homologous with ethyl, and give their formulæ.

774. Define ethers, hydrides, alcohols, ethereal salts, aldehyds.

775. What is the difference between homologous and heterologous series?

776. Give the systematic name of *fire-damp.*

777. Enumerate the chief constituents of coal-gas.

778. State the formulæ of formic, butyric, and valerianic acids.

779. Write the formulæ of butyl, its hydride, ether, alcohol, aldehyd, and acid.

METHYLIC ALCOHOL.

Methylic Alcohol (CH_3HO, or MeHO), Wood-Spirit, or Pyroxylic Spirit, or Wood-Naphtha, is a product of the destructive distillation of wood. Spirit of wine containing 10 per cent. of wood-spirit constitutes ordinary *methylated spirit*, a spirit issued duty free for the use of manufacturers, the methylic alcohol not interfering with technical applications. From its nauseous taste and odor, however, it cannot take the place of gin, brandy, or other spirit; hence, while industry is benefited, intemperance is discouraged and the revenue not injured.

Detection of Methylic Alcohol in Presence of Ethylic Alcohol. —Three or four methods have been proposed for the detection of methylated spirit in various liquids; that open to least objection is by J. T. Miller. For the application of the test to tinctures and similar spirituous mixtures, some of the spirit is first separated by distilling off a drachm or so from about half an ounce of the liquid placed in a small flask or test-tube having a long bent tube attached. Into a similar apparatus put 30 grains of powdered red chromate of potassium, half an ounce of water, 25 minims of strong sulphuric acid, and 30 or 40 minims of the spirit to be tested. Set the mixture aside for a quarter of an hour, and then distil nearly half a fluidounce. Place the distillate in a small dish, add a very slight excess of carbonate of sodium, boil down to about a quarter of an ounce, add enough acetic acid to impart a distinct but feeble acid reaction, pour the liquid into a test-tube, add a grain of nitrate of silver dissolved in about 30 drops of water, and heat gently for a couple of minutes. If the liquid then merely darkens a little, but continues quite translucent, the spirit is free from methylic alcohol; but if a copious precipi-

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Upward of fifty distinct chemical substances have been obtained from the solid, liquid, and gaseous products of the destructive distillation of coal.

tate of dark-brown or black metallic silver separates, and the tube, after being rinsed out and filled with clear water, has a distinct film of silver, which appears brown by transmitted light (best seen by holding it against white paper), the spirit is methylated.

Explanation.—This test depends for its action on the reducing powers of formic acid. In the above operation the ethylic alcohol becomes oxidized to acetic acid (the natural acid of the ethyl series), which does not reduce silver salts, a minute quantity only of formic acid being produced, while the methylic alcohol yields formic acid (the natural acid of the methyl series) in a comparatively large quantity. Aldehyd, which is also a reducing agent, is simultaneously produced, but removed in the subsequent ebullition with carbonate of sodium.

Methylated Sweet Spirit of Nitre.—The preparation of spirit of nitrous ether from methylated spirit is illegal in Great Britain. For the detection of methylic alcohol in this liquid, Mr. Miller suggests the following modification of the above process:—

Shake about an ounce of the sample with 20 or 30 grains of anhydrous carbonate of potassium, and, if needful, add fresh portions of the salt until it ceases to be dissolved, then pour off the supernatant spirit. This serves to neutralize acid and to remove water, of which an abnormal quantity may be present. Introduce half a fluidounce of the spirit into a small flask; add 150 grains of anhydrous chloride of calcium in powder, and stir well together; then, having connected the flask with a condenser, place it in a bath of boiling water and distil a fluidrachm and a half, or continue the distillation until scarcely anything more comes over. The operation is rather slow, but needs little attention, and should be done thoroughly. The distillate contains nearly the whole of the nitrous ether and other interfering substances, while in the retort there remains a non-volatile compound of chloride of calcium and methylic alcohol, if the latter be present. Now add to the contents of the flask a fluidrachm of water, which decomposes the compound just referred to, and draw over the half drachm of spirit required for testing. Add to it the usual oxidizing solution composed of 30 grains of red chromate of potassium, 25 minims of strong sulphuric acid, and half an ounce of water; let the mixture stand a quarter of an hour, then distil half a fluidounce. Treat the distillate with a slight excess of carbonate of sodium, boil rapidly down to two fluidrachms, and drop in, cautiously, enough acetic acid to impart a faint acid reaction; pour the liquid into a test-tube about three-quarters of an inch in diameter; add two drops of *diluted* acetic acid, and one grain of nitrate of silver in half a drachm of pure water; apply heat, and boil gently for two minutes. If the spirit is free from methylic alcohol, the solution darkens and often assumes transiently a purplish tinge, but continues quite translucent, and the test-tube, after being rinsed out and filled with water, appears clean or nearly so. But if the spirit contains only 1 per cent. of methylic alcohol, the liquid turns first brown, then almost black and opaque, and a film of silver, which is brown by transmitted light, is deposited on the tube. When the sample is methylated to the extent of 3 or 4 per cent., the film is sufficiently thick to form a brilliant mirror. To ensure accuracy, the experiments should be performed by daylight.

CHLOROFORM.

Formula $CHCl_3$.

Process.—Should the necessary appliances be at hand, a small quantity of this liquid may easily be prepared by the official process. One fluidounce and a half of spirit and 24 of water are placed in a retort or flask of at least a quart capacity; 8 oz. of chlorinated lime and 4 of slaked lime are added, the vessel connected with a condenser, and the mixture heated until distillation commences, the source of heat then being withdrawn. The condensed liquid should fall into a small flask containing water, at the bottom of which about a drachm of chloroform will slowly collect.

Explanation of the Process.—The hypochlorite of calcium believed to be present in the chlorinated lime (see the remarks in connection with the latter, p. 111) readily yields up oxygen and chlorine to organic substances, the calcium being liberated as hydrate, $4(Ca2ClO) + 4H_2O = 4(Ca2HO) + 2O_2 + 4Cl_2$. The alcohol used in making chloroform is thus reduced first to aldehyd:—

$$\underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

The action of chlorine on aldehyd then probably gives chloral (*chlor-al*dehyd):—

$$\underset{\text{Aldehyd.}}{C_2H_4O} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

The hydrochloric acid being at once neutralized by some of the liberated hydrate of calcium to form chloride of calcium and water, more freed hydrate of calcium and chloral gives formate of calcium and chloroform.

$$\underset{\text{Chloral.}}{2C_2HCl_3O} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Formate of}\\\text{calcium.}}}{Ca2CHO_2} + \underset{\text{Chloroform.}}{2CHCl_3}$$

Or, neglecting the probable steps in the process, and regarding only the materials and the products, 4 molecules of alcohol and 8 of hypochlorite of calcium give two of chloroform, 3 of formate of calcium, 5 of chloride of calcium, and 8 of water, thus:—

$$\underset{\text{Alcohol.}}{4C_2H_6O} + \underset{\substack{\text{Hypochlorite}\\ \text{of calcium.}}}{8CaCl_2O_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Formate of}\\ \text{calcium.}}}{3(Ca2CHO_2)} + \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{5CaCl_2} + \underset{\text{Water.}}{8H_2O}$$

The hydrate of calcium placed in the generating-vessels is not essential, but is useful in preventing secondary decompositions, the hydrate of calcium obtainable from the reaction being insufficient for this purpose.

Constitution.—Chloroform is sometimes considered to be the chloride of a trivalent radical formyl (CH), the first member of a series C_nH_{2n-1}. Glycerin is the hydrate of another member—*glyceryl*, C_3H_5 (p. 453).

Chloroform may also be regarded as the chloride of di-chlor-methyl; it may be formed from methylic compounds, thus:—

$$\underset{\substack{\text{Methylic}\\ \text{alcohol.}}}{2CH_4O} + \underset{\substack{\text{Chlorinated}\\ \text{lime.}}}{2(CaCl_2,CaCl_2O_2)} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Oxychloride of}\\ \text{calcium.}}}{CaCl_2 3CaO} + \underset{\text{Water.}}{3H_2O}$$

Chlorine converts it into tetrachloride of carbon, completing a series of *substitution products* of chloride of methyl.

$$\underset{\substack{\text{Chloride of}\\ \text{methyl.}}}{C\left\{\begin{matrix}H\\H\\H\end{matrix}\right\}Cl} \quad \underset{\substack{\text{Chloride of}\\ \text{mono-chlor-}\\ \text{methyl.}}}{C\left\{\begin{matrix}H\\H\\Cl\end{matrix}\right\}Cl} \quad \underset{\substack{\text{Chloride of}\\ \text{di-chlor-}\\ \text{methyl.}}}{C\left\{\begin{matrix}H\\Cl\\Cl\end{matrix}\right\}Cl} \quad \underset{\substack{\text{Chloride of}\\ \text{tri-chlor}\\ \text{methyl.}}}{C\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}Cl} \quad \underset{\text{or}}{\text{or}} \quad \underset{\substack{\text{Tetrachlo-}\\ \text{ride of}\\ \text{carbon.}}}{CCl_4}$$

The chloride of mono-chlor-methyl, under the name of dichloride of methylene, has been used as an anæsthetic. It may be obtained by the action of nascent hydrogen on chloroform.

Chloroform is purified by shaking it with pure sulphuric acid containing no trace of nitric acid, which chars and removes hydrocarbons, etc., but does not affect chloroform. It is freed from any trace of acid by agitation with carbonate of sodium, and from moisture by distillation with lime.

Properties.—The sp. gr. of purified chloroform is 1.500. It is liable to slowly decompose when exposed to air and light. To render it stable a minute amount of alcohol (one-tenth of 1 per cent.—0.1, or at most 1 per cent.) is necessary; hence the specific gravity of medicinal chloroform is about 1.497 (1.485 to 1.490, *Chloroformum Purificatum*, U. S. P.). It readily and entirely volatilizes at common temperatures, having, to the last drop, its pleasant characteristic odor. It has a sweetish taste, is limpid, colorless, soluble in alcohol (1 to 9 gives *Spiritus Chloroformi*, U. S. P.) and ether, and slightly in water. It burns with a sluggish green smoky flame. It should be neutral to test-paper, indicating absence of acid; give no precipitate with solution of nitrate of silver, indicating absence of ordinary chlorides; remain colorless when heated with potash, indicating absence of aldehyd; and give no color to any sulphuric acid with which it may be shaken, even after the mixture has been set aside for half an hour, indicating absence of hydrocarbons, etc. Alcohol may be detected by Lieben's test (p. 429), or by shaking with a little of the dye termed "Hofmann's violet," which gives the chloroform a purple tint if alcohol be present, but affords no color with pure chloroform.

Commercial Chloroform (*Chloroformum Venale*, U. S. P.) should have a sp. gr. "not lower than 1.470 at 15° C."

Aqua Chloroformi, B. P., the official chloroform-water, is made by shaking 1 fluidrachm of chloroform with 25 ounces of distilled water till dissolved.

IODOFORM (*Iodoformum*, U. S. P.), analogous in constitution to chloroform, the iodine taking the place of the chlorine (CHI_3), may be prepared by mixing in a retort 2 parts of crystallized carbonate of sodium, 1 to 2 parts of iodine, 1 part of alcohol, and 10 of water, heating at about 150° F. till colorless, and then pouring into a beaker and allowing to settle. The iodoform is deposited in yellow scales, which are collected on a filter, washed thoroughly with water, and dried between filtering-paper.

Iodoform appears in the shape of yellow, shining six-sided scales with a saffron-like odor; is volatile at ordinary temperatures, and at a temperature above 250° is decomposed, giving off violet vapors. Almost insoluble in water, but more so in alcohol, ether, and the fixed and volatile oils. Sp. gr. 2.000.

CHLORAL AND CHLORAL HYDRATE.

Process.—Pass a rapid stream of dry chlorine into pure absolute alcohol so long as absorption occurs. During the first hour or two the alcohol must be kept cool, afterward gradually warmed till ultimately the boiling-point is reached. The preparation of a considerable quantity occupies several days. The crude product is mixed with three times its volume of oil of vitriol and distilled, again mixed with a similar quantity of oil of vitriol, and again distilled, and finally rectified from quicklime.

The formation of chloral would at first sight seem to be due to the production from the alcohol (C_2H_6O) of aldehyd (C_2H_4O), through the removal of hydrogen by the chlorine and the substitution of chlorine for hydrogen in the aldehyd (C_2H_4O), with formation of *chlor-aldehyd* or *chloral* (C_2HCl_3O). But the reactions are far more complicated, being somewhat as follows: Aldehyd and hydrochloric acid are first formed; these with some of the alcohol give monochlorinated ether, $\left.\begin{matrix}C_2H_5\\C_2H_4Cl\end{matrix}\right\}O$, which with more chlorine yields tetrachlorinated ether, $\left.\begin{matrix}C_2H_5\\C_2HCl_4\end{matrix}\right\}O$, and this in presence of water furnishes chloral, some alcohol, and some hydrochloric acid (Wurtz and Vogt).

Properties.—The formula of chloral is C_2HCl_3O. It is a colorless liquid, of oily consistence. Sp. gr. 1.502. Boiling-point 201.2° F. Its vapor has a penetrating smell, and is somewhat irritating to the eyes. Mixed with water, heat is disengaged, and solid white, crystallizable *hydrous chloral* (*Chloral*, U. S. P.), or, what is more generally, though somewhat irregularly, termed *chloral hydrate* (C_2HCl_3O,H_2O) or *hydrate of chloral* (*Chloral Hydras*, B. P.), results. The latter fuses at 110.8°, and boils at 95° C. or 203° F. It sublimes as a white crystalline powder. Both chloral and chloral hydrate are soluble in water, alcohol, ether, and oils. Oils and fats are also soluble in chloral hydrate. The aqueous solution should be neutral, and give no reaction with nitrate of silver. Chloral, especially if it contains a trace of acid, may undergo a spontaneous change into an opaque, white isomeric modification (metachloral), insoluble in water, alcohol, or ether, but convertible by prolonged contact with water or by distillation into the ordinary condition. By action of weak alkalies chloral first yields formate of the alkali-metal and chloroform :—

$$C_2HCl_3O + KHO = KCHO_2 + CHCl_3.$$

Chloral, or rather strong aqueous solution of chloral hydrate (3 in 4), injected beneath the skin yields nascent chloroform by action of the alkali of the blood, and produces narcotic effects (Liebreich, Personne). Chloroform itself admits of similar hypodermic use (Richardson). If administered by the stomach, 30 to 80 grains of solid hydrate are required. The final products of the reaction of the chloroform and blood are formate and chloride of sodium. A spirituous solution of potash effects the same transformation.

$$CHCl_3 + 4KHO = KCHO_2 + 3KCl + 2H_2O.$$

Solution of ammonia and moist hydrate of calcium, as well as weak solutions of fixed alkalies, convert hydrate of chloral into formate of the metal and chloroform. The reaction with the slaked lime being especially definite and complete (Wood), it may be employed in ascertaining the richness of a sample of commercial chloral hydrate in chemically pure chloral hydrate.

$$\underbrace{2(C_2HCl_3O,H_2O)}_{331} + Ca2HO = \underbrace{2CHCl_3}_{239} + Ca2CHO_2 + 2H_2O.$$

From the foregoing equation and molecular weights it is obvious that 100 grains of hydrate of chloral, if quite dry, will yield by distillation with 30 grains of slaked lime and an ounce of distilled water (in a small flask and long bent tube kept cool by moistened paper) 72.2 grains of chloroform by weight or (the sp. gr. of chloroform being taken at 1.497) 47.56 grains by measure, or about 52 minims. One hundred grains of the official hydrate of chloral "should yield not less than 70 grains of chloroform."

Pure Chloral Hydrate.—Liebreich, who first proposed the use of chloral hydrate, gives the following as the characteristics of a pure article: Colorless, transparent crystals. Does not decompose by the action of the atmosphere, does not leave oily spots when pressed between blotting-paper, affects neither cork nor paper. Smells agreeably aromatic, but a little pungent when heated. Taste bitter, astringent, slightly caustic. Seems to melt on rubbing between the fingers. Dissolves in water like candy without first forming oily drops, and the solution is neutral or faintly acid to test-paper. Dissolves in bisulphide of carbon, petroleum, ether, water, alcohol, oil of turpentine, etc. Its solution in chloroform gives no color when shaken with sulphuric acid. Boiling-point 203° to 205° F., and volatilizes without residue. Distilled with sulphuric acid, the chloral should pass over at 205° to 207° F. Melting-point 133° to 136° F., again solidifying at about 120° F. Gives no chlorine reaction on treating the solution in water (acidulated by nitric acid) with nitrate of silver.

Impure Chloral Hydrate.—Yellowish, cloudy. Decomposes; leaves spots by pressing between blotting-paper; decomposes corks and paper of the packing. Smells pungent and irritating; on opening the bottles sticky and often emits fumes. Taste strongly caustic. With water forms oily drops or is partially insoluble. Boils at a higher temperature. On treating it with sulphuric acid turns brown, with formation of hydrochloric acid. Gives chlorine reaction on treating the solution in water (acidulated by nitric acid) with nitrate of silver.

Alcoholates of chloral are obtained on combining alcohols with chloral. They are more soluble in chloroform than the hydrate, which dissolves to the extent of 1 in 4.

Bromal (C_2HBr_3O), *hydrate of bromal* (C_2HBr_3O,H_2O), and *alcoholates of bromal* are produced when bromine itstead of chlorine attacks alcohol. *Iodal* (C_2HI_3O) also exists.

Butyl chloral ($C_4H_5Cl_3O$), originally but erroneously termed *croton chloral*, is a product of the action of chlorine on aldehyd. Its name expresses its constitution; it is *chlorinated butyric aldehyd*, ordinary chloral being chlorinated vinic aldehyd.

AMYLIC ALCOHOL.

Amylic Alcohol (*Alcohol Amylicum*, B. P.) ($C_5H_{11}HO$, or AyHO) is a constant accompaniment of ethylic or common alcohol (C_2H_5HO, or EtHO) when the latter is prepared from sugar which has been derived from starch; hence the name, from *amylum*, starch. The sugar of potato-starch yields a considerable quantity; hence the alcohol is often called *potato oil.* It is also termed *fousel oil*, or *fusel oil* (from *φυω*, *phuō*, to produce), in allusion to the circumstance that the supposed oil is not simply educed from a substance already containing it, as is usually the case with oils, but is actually produced during the operation. It was described as oil, probably because it resembled oil in not readily mixing with water; but it is soluble to some extent in water, and is a true spirit, homologous with spirit of wine. It often contains variable proportions of propylic, butylic, and caproylic alcohols. See also Valerianic Acid.

Amylic alcohol is a "colorless liquid, with a penetrating and oppressive odor, and a burning taste. When pure its specific gravity is 0.818; boiling-point 279° F. Sparingly soluble in water, but soluble in all proportions in alcohol, ether, and essential oils. Exposed to the air in contact with platinum-black, it is slowly oxidized, yielding valerianic acid." Two allotropic varieties of amylic alcohol exist, one dextro-rotating a polarized ray. The amylic alcohol of trade probably contains both varieties.

ACETATE OF AMYL ($C_5H_{11}C_2H_3O_2$, or $Ay\overline{A}$).—To a small quantity of amylic alcohol in a test-tube add some acetate of potassium and a little sulphuric acid, and warm the mixture; the vapor of acetate of amyl is evolved, recognized by its odor, which is that of the jargonelle pear. If a condensing-tube be attached, the essence may be distilled over, washed by agitation with water to free it from alcohol, and separated by a pipette.

$$\underset{\substack{\text{Acetate of}\\\text{potassium.}}}{K\overline{A}} + \underset{\substack{\text{Amylic}\\\text{alcohol.}}}{AyHO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Acetate of}\\\text{amyl.}}}{Ay\overline{A}} + \underset{\substack{\text{Acid sulphate}\\\text{of potassium.}}}{KHSO_4} + \underset{\text{Water.}}{H_2O}$$

Fruit-Essences.

Acetate of amyl, prepared with the proper equivalent proportions of constituents as indicated by the above equation, is largely manufactured for use as a flavoring agent by confectioners. Valerianate of amyl ($C_5H_{11}C_5H_9O_2$) is similarly used under the name of apple oil. Butyrate of ethyl ($C_2H_5C_4H_7O_2$) closely resembles the odor and flavor of the pineapple; œnanthylate of ethyl ($C_2H_5C_7H_{13}O_2$) recalls green gage; pelargonate of ethyl ($C_2H_5C_9H_{17}O_2$) quince; suberate of ethyl ($Et_2C_8H_{12}O_4$) mulberry; sebacate of ethyl ($Et_2C_{10}H_{16}O_4$) melon. Hydride of salicyl ($C_7H_5O_2H$), or salicylous acid, is the essential oil of meadow-sweet (*Spiræa ulmaria*), and may be prepared artificially by the oxidation of salicin (*vide* p. 423). Acid salicylate of methyl ($CH_3HC_7H_4O_3$), or gaultheric acid (*Oleum Gaultheriæ*, U. S. P.), forms the chief part of the essential oil of the leaves (*Gaultheria*, U. S. P.) of wintergreen (*Gaultheria procumbens*, the fresh leaves of which yield an average of 0.4 per cent. of oil), and may also be prepared artificially from salicin. Salicylic acid ($C_7H_6O_3$ or $H_2C_7H_4O_3$) can easily be obtained from the salicylate of methyl, but more cheaply from carbolic acid. (*Vide* p. 451.)

When heated to about 80° C. (176° F.) the oil should not yield a colorless distillate having the characteristics of chloroform or of alcohol. On mixing 5 drops of the oil with 5 drops of nitric acid, the mixture should not acquire a deep-red color, and should not solidify to a dark-red, resinous mass (abs. of oil of sassafras).

By mixing ethereal salts with each other and with essential oils in various proportions the odor and flavor of nearly every fruit may be fairly imitated. (For a set of formulæ of fruit-essences, see the *Pharmaceutical Journal*, May 17, 1879.)

Nitrite of Amyl.

NITRITE OF AMYL (*Amyl Nitris*, U. S. P.) ($C_5H_{11}NO_2$).—For the preparation of this substance Maisch recommends a modification of

Balard's process. Amylic alcohol is first rectified until pure; that is, until its boiling-point is about 270° F. This alcohol, with about an equal bulk of nitric acid, is introduced into a capacious glass retort, and a moderate heat is applied and very gradually increased. As soon as the mixture approaches boiling the fire is removed, and the reaction allowed to continue. If the application of the heat has been too rapid or too long continued, considerable frothing occurs and the contents of the retort are apt to foam over. With a moderate and slowly increased heat the reaction is less violent, and the temperature rises gradually after the removal of the fire and the beginning of boiling. As soon as the thermometer, inserted in the tubulure, rises above 212° F., the receiver is changed, the distillate now becoming more and more mixed with ethyl-amylic ether and nitrate of amyl, readily perceived by the change in odor.

The distillate obtained below 212° F. is agitated with an aqueous solution of hydrate or carbonate of potassium to remove free acids, and, after separation, the oily liquid is introduced into a clean retort and again slowly heated. The first portion coming over contains amylic aldehyd. When the very slowly increased heat has risen to 205° F., the receiver is again changed, and the distillate now collected as nitrite of amyl, until the thermometer reaches 212° F., when the distillation is stopped.

Nitrite of amyl is a yellowish ethereal liquid; sp. gr. of liquid is about 0.873, of vapor 4.03; boiling-point 205° F.; soluble in spirit of wine, insoluble in water; converted by fused caustic potash into valerianate of potassium. Exposed to air, it yields amylic alcohol.

QUESTIONS AND EXERCISES.

780. Name the source of methylic alcohol.

781. What is "methylated spirit"?

782. Describe the method by which methylated spirit is detected in a tincture.

783. In what relation does formic acid stand to methylic alcohol?

784. How would you proceed to ascertain whether or not a specimen of sweet spirit of nitre had been made from methylated spirit?

785. Give details of the production of chloroform from alcohol, tracing the various steps by equations.

786. Is chloroform an ethylic compound? What is its probable constitution?

787. How is chloroform purified?

788. State the character of pure chloroform.

789. Describe the reactions that occur in the manufacture of chloral and chloral hydrate.

790. What is the nature of the action of alkalies on chloral hydrate?

791. Mention the characters of pure and impure chloral hydrate.

792. Whence is amylic alcohol obtained?

793. Has valerianic acid any chemical relation to amylic alcohol?

794. Mention the systematic names of several artificial fruit-essences.

795. What is the formula of nitrite of amyl, and how is it prepared?

SALTS AND DERIVATIVES OF RADICALS OF OTHER SERIES THAN THE C_nH_{2n+1}.

What has been stated regarding radicals having the general formula C_nH_{2n+1} and their salts may be applied to the radicals of other series.

The series C_nH_{2n-7} includes *phenyl* (C_6H_5), the so-called hydride of which (C_6H_5H, or PhH) is common *benzol* or *benzene* (B. P.), a colorless volatile liquid distilled from coal-tar, and a body which in constitution is the type of a very large class of aromatic organic bodies. *Toluol* (C_7H_8), or methyl benzol, is one of the products of the distillation of balsam of Peru. The next homologue, *xylol* (C_8H_{10}), or dimethyl-benzol, is contained in crude wood-spirit and in coal-naphtha: it is a colorless fluid, having an odor faintly resembling that of benzol; boiling-point 282° F.; sp. gr. .866.

Benzol is a powerful solvent of grease, and under the name of *Benzene Collas* was introduced by M. Collas in 1848 for cleansing stuffs.* By the action of strong nitric acid benzol yields *nitrobenzol* ($C_6H_4(NO_2)H$), a liquid termed, from its odor, *artificial oil of bitter almonds*, or *essence of mirbane.* Its specific gravity is 1.20 to 1.29. The odor of this essence, however, is not exactly that of essential oil of almonds, and its composition is very different, so that it is not truly an artificial volatile oil. The natural oil has a sp. gr.

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* The light product of the distillation of petroleum is also, unfortunately, termed *benzine, benzin, benzoline* (*Benzin*, U. S, P., *Petroleum Benzin, Petroleum Ether.* C_5H_{12}, C_6H_{14}, and other hydrocarbons of the marsh-gas series. Boiling-point 50° to 60° C., 122° to 140° F.). It requires five or six times its bulk of alcohol for solution, while benzol dissolves in less than its own bulk. Sp. gr. of benzol, about .9; of benzin, 0.670 to 0.675. Benzin, when evaporated upon the hand, should leave no odor, and when evaporated in a warm dish should leave no residue (abs. of heavy hydrocarbons). When boiled a few minutes with one-fourth its volume of spirit of ammonia and a few drops of test-solution of nitrate of silver, the ammoniacal liquid should not turn brown (abs. of pyrogenous products and sulphur compounds).

The heavier, semi-solid purified product ($C_{16}H_{34}$, etc.) of the distillation of petroleum, melting between 40° C. and 51° C., is officially (U. S. P.) termed *Petrolatum* or *Petroleum Ointment.* In trade it is known as one of the varieties of *Vaseline.*

If 5 gm. of Petroleum Ointment be digested, for half an hour, with 5 gm. of soda and 25 gm. of water, the aqueous layer separated, and supersaturated with diluted sulphuric acid, no oily substance should separate (abs. of fixed oils or fats of vegetable or animal origin, or of resin). Liquefied Petroleum Ointment agitated with sulphuric acid of sp. gr. 1.540 should not acquire a dark color within two hours (abs. of readily carbonized organic impurities).

of 1.04 to 1.07, and is a hydride of the negative radical[*] benzoyl (C_7H_5OH), a radical derived from the next higher homologue of phenyl by displacement of hydrogen by oxygen. Nitrobenzol yields aniline (*vide infra*), oil of bitter almonds does not (page 417). On this reaction the test for nitrobenzol is founded (p. 451). *Dinitrobenzol* ($C_6H_3(NO_2)_2H$) may also be obtained.

The hydrate of phenyl (C_6H_5HO), or *phenic alcohol* or *phenol*, is the *phenic acid* or *carbolic acid* ($H_2C_6H_4O$) of commerce (*Acidum Carbolicum*, U. S. P.), a colorless crystalline substance obtained from coal-tar oil by fractional distillation between 180° and 190° C., and subsequent purification. A crystalline hydrous acid ($H_2C_6H_4O,H_2O$) may also be obtained. At temperatures above 95° F. ordinary carbolic acid is an oily liquid. It is only slightly soluble in water, but readily dissolved by alcohol, ether, and glycerin. In odor, taste, and solubility (and in appearance when liquefied by heat or by the addition of 5 per cent. of water) it resembles creasote, a wood-tar product for which carbolic acid has been substituted. Besides hydrate of phenyl (C_6H_5HO), coal-tar oil contains *cresol*, *hydrate of cresyl*, or cresylic acid (C_7H_7HO), while wood-tar oil furnishes *guaiacol* ($C_7H_8O_2$) —also a product of the destructive distillation of guaiacum resin— and *creasol* ($C_8H_{10}O_2$), or creasote. Certain coloring-matters may be obtained by the oxidation of carbolic acid; ammonia, or, still better, phenyl-ammonia (aniline) mixed with it, and then a small quantity of solution of a hypochlorite, gives a blue liquid; a similar effect is produced on dipping a chip of deal into carbolic acid (or into creasote), then into hydrochloric acid, and afterward exposing it to the air. By the following tests carbolic acid may be distinguished from creasote: The former boils only at 370° F., while the latter readily dries up at 212°. Carbolic acid does not affect a ray of polarized light; creasote twists it slightly to the right. Carbolic acid is either solid or may be solidified by cooling; creasote is not solidified by the cold produced by a mixture of hydrochloric acid and sulphate of sodium. Creasote from coal (impure or crude carbolic acid) gives a jelly when shaken with albumen or with collodion; creasote from wood (*Creasotum*, U. S. P.) is unaffected. Coal-creasote is soluble in solution of potash and in the strongest solution of ammonia (Read), wood-creasote scarcely soluble. The coal product is soluble in 20 volumes of water, and a neutral solution of ferric chloride strikes a permanent blue color with the liquid; wood-creasote is less soluble (*Aqua Creasoti*, U. S. P., is said to contain 1 in 129) and not permanently colored blue by ferric chloride. An alcoholic solution of the coal oil is colored brown by ferric chloride, a similar solution of true creasote green. "If 1 volume of creasote be mixed with 1 volume of glycerin, a nearly clear mixture will result, from which the creasote will be separated by the addition of 1 or more volumes of water." —U. S. P. Aqueous solution of carbolic acid gives a white precipitate with bromine-water.

Carbolic acid is a powerful *antiseptic* (ἀντὶ, *anti*, against, and σήπω,

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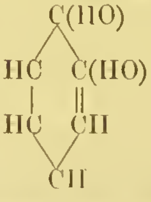
[*] *Negative* basylous organic radicals are derived from the ordinary or *positive* basylous organic radicals by displacement of two atoms of hydrogen in the latter radicals by one atom of oxygen.

sepo, I putrefy). In large doses it is poisonous, *antidotes* being a mixture of olive oil and castor oil, freely administered, or a mixture of slaked lime with about three times its weight of sugar rubbed together with a little water. *Acidum Carbolicum Crudum*, U. S. P., is the impure carbolic acid obtained from coal-tar by treating it first with an alkali, and then with an acid, and finally distilling. It is of a brown shade, and if at first colorless it becomes reddish-brown on pressure. It consists of carbolic and cresylic acids in variable proportion, together with impurities derived from coal-tar: 950 measures of warm water on being agitated with 50 measures of the liquid will dissolve out the two acids, and should not leave more than 5 measures of impurity (10 per cent.). Carbolic acid is soluble in oil of vitriol, *sulphocarbolic acid* ($HC_6H_5SO_4$) or *sulphophenic acid* being formed. On diluting and mixing with oxides, hydrates, or carbonates, *sulphocarbolates* are formed. The formula of *sulphocarbolate of sodium* (*Sodii Sulphocarbolas*, U. S. P.) is $NaC_6H_5SO_4,2H_2O$; *sulphocarbolate of zinc*, $Zn(C_6H_5SO_4)_2H_2O$. Trinitro-carbolic acid ($C_6H_3(NO_2)_3O$) is formed on slowly dropping carbolic acid into fuming nitric acid; it is the yellow dye known as *carbazotic acid* or *picric acid;* most of the picrates are explosive by percussion. Both carbolic acid and benzol are secondary products obtained in the manufacture of coal-gas; hence, indeed, the word *phenic*, and thence *phenyl* (from *φαίνω*, *phaino*, I light, in allusion to the use of coal-gas).

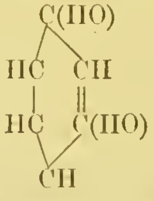
Carbolic acid (C_6H_5HO) may be regarded as benzol in which one atom of hydrogen (H) is displaced by hydroxyl (HO). When two atoms of hydrogen in benzol are displaced by two of hydroxyl, *resorcin* (C_6H_42HO) results, a colorless, crystalline antiseptic having many advantages over carbolic acid in surgical operations. Its name was given in allusion to its original source, resin, and to certain similarities with orcin. It occurs in flat prisms readily soluble in most liquids. It may be made by passing benzol vapor into hot sulphuric acid and heating the product (benzol-disulphonic acid, $C_6H_4(SO_2,HO)_2$) with excess of soda.

$$\underset{\substack{\text{Benzol-disulphonate}\\\text{of sodium.}}}{C_6H_4(SO_2.NaO)_2} + \underset{\text{Soda.}}{2NaHO} = \underset{\text{Resorcin.}}{C_6H_4(HO)_2} + \underset{\substack{\text{Sulphite of}\\\text{sodium.}}}{2Na_2SO_3}$$

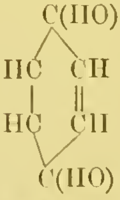
Resorcin is one of a group of three metameric dihydroxyl-benzols (C_6H_42HO). Their chemical relationships warrant the conclusion (on the atomic theory) that the cause of their differences in properties is a difference of position of the two atoms of hydroxyl in the molecule, these being, respectively, next to each other, separated by one atom (of CH) and by two atoms of CH), thus:—



Ortho-dihydroxyl-benzol (pyrocatechin).



Meta-dihydroxyl-benzol (resorcin).



Para-dihydroxyl-benzol (hydroquinone).

Aniline, or *phenylamine*, is a product of the action of nascent hydrogen on nitrobenzol.

$$\underset{\text{Nitrobenzol.}}{C_6H_5NO_2} + \underset{\text{Hydrogen.}}{3H_2} = N\left\{\begin{matrix} C_6H_5 \\ H \\ H \end{matrix}\right. + 2H_2O,$$

the substance whence, by oxidation, etc. aniline-red (magenta), -orange, -yellow, -green, -blue, -violet (mauve), and -black are produced. The process with zinc-dust (*vide* Watt's Dict.) answers fairly well: 1 oz. of nitrobenzol gives a drachm or two of aniline. But action of iron filings and acetic acid on an alcohol solution answers better, 3 oz. of nitrobenzol giving 1 oz. of aniline. To detect nitrobenzol add alcohol and hydrochloric acid and a little zinc; when action has ceased, liberate aniline by shaking with excess of potash; dissolve out the aniline by agitation with ether; to the decanted ethereal liquid add solution of chlorinated lime; a violet color or tint results.

Salicylic Acid ($H_2C_7H_4O_3$) (*Acidum Salicylicum*, U. S. P.).—The natural acid salicylate of methyl is described on page 446. Salicylic acid itself occurs in several species of violet (Mandelin), especially in *Pansy* (*Viola Tricolor*, U. S. P.). Artificial salicylic acid is made as follows: Carbolic acid ($H_2C_6H_4O$), by acquiring the elements of carbonic acid gas (CO_2), is converted into salicylic acid (Kolbe). The carbolic acid is first mixed with caustic soda in molecular proportions and dried. The resulting acid carbolate of sodium ($NaHC_6H_4O$), made hot, is saturated with carbonic gas, every pair of molecules of the carbolate then affording one of regenerated carbolic acid, which distils off, and one of normal carbolate of sodium ($Na_2C_6H_4O$) which, absorbing the gas, becomes normal salicylate of sodium ($Na_2C_7H_4O_3$). The latter, by action of hydrochloric acid, furnishes salicylic acid, which may be purified by crystallization from ethylic or amylic alcohol or ether. Salicylic acid, like carbolic acid, is a powerful antiseptic, but is free from the taste and smell of carbolic acid. It is only slightly soluble in water, but readily soluble in aqueous solutions of such alkali-metal salts as borax, phosphate of sodium, or citrate of potassium. A similar antiseptic, *cresotic acid* ($C_8H_8O_3$), is similarly obtained from cresylic acid (C_7H_8O). Ferric chloride strikes a violet coloration with both salicylic and cresotic acids. Both acids have antipyretic powers. The true salicylates of the alkali-metals, and probably, therefore, the cresotates, are very feeble antiseptics. Salicylate of sodium (*Sodii Salicylas*, U. S. P.), $2NaC_7H_5O_3,H_2O$, is fairly soluble in water. Carbolic acid often containing cresylic acid, commercial salicylic acid may often contain cresotic acid. Salicylic acid is soluble in strong sulphuric acid, yielding colorless *sulphosalicylic acid* ($HC_7H_5O_2SO_4$). Salicylic acid yields colored substances on being nitrated and etherified, etc. If it affords a reddish or brownish tint when its aqueous solution is shaken with chlorate of potassium and hydrochloric acid, and, afterward, ammonia, carbolic acid is present.

Aloins.—The aloes (*Aloe*, U. S. P.) of pharmacy (from *Aloe Socotrina*) is an evaporated juice, doubtless much altered by the temperature to which it is subjected. *Aloe Purificata*, U. S. P., is the evaporated alcoholic extract.

Barbaloin.—This substance, first obtained by T. and H. Smith, occurs in minute crystals in Barbadoes aloes. It is readily procured by making a decoction in water acidified with a little hydrochloric acid, after some hours pouring off the precipitated resin, and evaporating the liquid to a syrup. The aloin crystallizes out in a day or two. Barbaloin yields by the action of bromine and chlorine substitution compounds. Nitric acid dropped upon it produces a red color which soon fades. Boiled for some time with strong nitric acid, barbaloin gives, together with oxalic and picric acids, a yellow substance, chrysammic acid, which furnishes beautiful red salts (Tilden). Anthracene ($C_{14}H_{10}$) has been obtained by deoxidation of barbaloin.

Nataloin.—This body was discovered by Flückiger in Natal aloes. It crystallizes readily in rectangular plates, either from spirit or from water. No bromine or chlorine substitution derivatives have yet been formed, but an acetyl compound has been analyzed (Tilden). Nataloin moistened with nitric acid gives a red coloration which does not fade. When boiled with nitric acid it yields no chrysammic acid, but only oxalic and picric acids.

Socaloin, or *Zanaloin.*—Histed and Flückiger have shown that Socotrine or Zanzibar aloes yields an aloin distinct from those just described. It forms tufted acicular prisms. Nitric acid scarcely alters the color of socaloin. Neither socaloin nor barbaloin affords any color when vapor from a glass rod moistened with nitric acid is brought near to a drop of oil of vitriol containing a minute fragment of the aloin, while nataloin gives rise to a blue coloration.

Analysis.—To Aloin, or powdered aloes, on a white plate, add strong nitric acid. *No color* = *Socaloin: crimson color* = Nataloin or Barbaloin. To another portion add strong sulphuric acid and vapor of nitric acid. *A blue color* = Nataloin; *no blue color* = Barbaloin.

Formulæ.—The reactions of these bodies seem to indicate that they are complex phenols. Phenol being the phenyl hydrate, C_6H_5HO, and cresol being methyl-phenol, $C_6H_4CH_3HO$, the aloins may possibly have a similar constitution; that is, they may be the hydrates of radicals in which part of the hydrogen is replaced by groups of atoms. Since Tilden made this suggestion, E. von Sommaruga and Egger (*Pharmacographia*) have arrived at the conclusion that the aloins form an homologous series, and that they have the composition indicated in the following formulæ:—

Socaloin	$C_{15}H_{16}O_7$
Nataloin	$C_{16}H_{18}O_7$
Barbaloin	$C_{17}H_{20}O_7$

Tilden's more recent experiments indicate, however, that barbaloin ($C_{17}H_{20}O_7$) and socaloin ($C_{15}H_{16}O_7$) are isomeric in the anhydrous state, but that socaloin and its derivatives in the hydrous condition contain more water of crystallization than barbaloin. Nataloin ($C_{16}H_{18}O_7$) seems to be isomeric with the others, but is less soluble, and does not yield either chrysammic acid or chloro- or bromo-derivatives ($C_{16}H_{15}Cl_3O_7$; $C_{16}H_{15}Br_3O_7$). The acetyl derivative appears to have the formula $C_{16}H_{15}(C_2H_3O)_3O_7$.

In the series $C_nH_{2n-1}{}'$ we have the univalent radical *allyl* (C_3H_5), whose sulphide ($(C_3H_5)_2S$) is *essential oil of garlic* (*Allium*, U. S. P.), and sulphocyanate (C_3H_5CyS), the chief part of the *essential oil of mustard*, the body to which mustard owes its power of inducing inflammatory action on the skin ("Mustard Poultice" and *Charta Sinapis*, U. S. P.). *Mustard* (*Sinapis*, U. S. P.) is a powdered mixture of black, or rather reddish-brown, and white mustard-seeds. The white mustard-seed contains *sinalbin* ($C_{30}H_{44}N_2S_2O_{16}$), a glucoside which, in contact with the myrosin in an aqueous extract of mustard, yields the sulphocyanide of a peculiar radical *acrinyl*, a body which forms part of the essential oil of mustard-paste.

$$\underset{\text{Sinalbin.}}{C_{30}H_{44}N_2S_2O_{16}} = \underset{\substack{\text{Sulphocyanate}\\ \text{of acrinyl.}}}{C_7H_7OCNS} + \underset{\substack{\text{Acid sulphate}\\ \text{of sinapine.}}}{C_{16}H_{24}O_5NSHSO_4} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

The black contains the albumenoid ferment *myrosin*, resembling the *emulsin* of almonds (p. 416), and *myronate* of potassium or *sinigrin*. The latter is the body which, under the influence of the former, yields the chief part of the pungent oil of mustard-paste.

$$\underset{\substack{\text{Myronate of}\\ \text{potassium.}}}{KC_{10}H_{18}NS_2O_{10}} = \underset{\substack{\text{Acid sulphate}\\ \text{of potassium.}}}{KHSO_4} + \underset{\substack{\text{Oil of}\\ \text{mustard.}}}{C_3H_5CNS} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

Crude oil of mustard often contains *cyanide of allyl*, C_3H_5CN.

In the Pharmacopœia of India the seed of *Sinapis juncea Rai*, or *Indian Mustard-Plant*, is official in addition to that of *S. alba* and *S. nigra*. It is the common mustard of warm countries. It does not differ chemically from other mustard. Allyl compounds are also met with in several other cruciferous and liliaceous plants.

In the C_nH_{2n} series occurs *ethylene* or *olefiant gas* (C_2H_4), the chief illuminating constituent of coal-gas (made by heating spirit of wine with twice its volume of strong sulphuric acid), a bivalent radical, the alcohol of which is *glycol* (C_2H_42HO). *Etherol*, or *Ethereal Oil* (*Oleum Æthereum*, U. S. P.), a mixture of equal volumes of ether and of *heavy oil of wine* ($C_{15}H_{30}$?), a hydrocarbon polymeric with olefiant gas, is one of the products of the action of excess of sulphuric acid on alcohol; its sp. gr. is 0.917. In $C_nH_{2n-1}{}'''$ series the trivalent hypothetical radical *glyceryl* (C_3H_5) is found, the hydrate of which (C_3H_53HO) is glycerin. The homologues of glycol (*e. g.*, propylene glycol and butylene glycol) are termed *glycols*, the homologues of glycerin *glycerins*. By oxidation of glycols, acids of the lactic series are formed (glycolic, lactic, and oxybutyric acids), just as by oxidation of ordinary alcohols acids of the acetic series are formed. It will be noticed that the chemical composition of the radicals glyceryl and allyl is identical (C_3H_5), but the former is trivalent and the latter univalent; hence they probably differ in physical constitution; they are isomeric, possibly polymeric with each other. From a glyceryl compound (glycerin), however, an allyl salt (iodide) can be produced. By distilling a mixture of glycerin and biniodide of phosphorus, iodide of allyl (C_3H_5I) is obtained, and on digesting this with sulphocyanate of potassium the sulphocyanate of allyl, or *artificial oil of mustard*, results; identical with the chief constituent of the natural oil.

GLYCERIN.—Glycerin, or Glyceric Alcohol (C_3H_53HO), is the hydrate of the basylous radical of most oils and fats, bodies which are mainly oleates, palmitates, and stearates of glyceryl (glycyl or propenyl). When these substances are heated with metallic hydrates (even with water—hydrate of hydrogen—at a temperature of 500° F. or 600° F.), double decomposition occurs, oleate, palmitate, or stearate of the metal is formed, and hydrate of glyceryl, or glycerin. Hence glycerin is a by-product in the manufacture of soap, hard candles, and lead-plaster (*vide* Index).

Properties.—Glycerin is viscid when pure; specific gravity 1.28 (not below 1.25 U. S. P. = 95 per cent.); has a sweet taste; is soluble in water or alcohol in all proportions. It has remarkable powers as a solvent, is a valuable *antiseptic* even when diluted with 10 parts of water, and useful as an emollient. *In vacuo* it may be distilled unchanged, but under ordinary atmospheric pressure it is decomposed by heat. From damp air glycerin absorbs moisture slowly, but in considerable proportions. Perfectly pure and anhydrous glycerin, at a few degrees below the freezing-point of water, sometimes solidifies to a mass of crystals. It may be extracted from many substances insoluble in absolute alcohol by digestion in the latter, acids being first neutralized by oxides and oxides and hydrates by acids.

"Glycerin should be neutral to litmus-paper. Upon warming a portion of 5 or 6 gm. with half its weight of diluted sulphuric acid, no butyric or other acidulous odor should be developed. A portion of 2 or 3 gm., gently warmed with an equal volume of sulphuric acid in a test-tube, should not become dark colored (abs. of cane-sugar). A portion of about 2 gm., heated in a small, open porcelain or platinum capsule upon a sand-bath until it boils, and then ignited, should burn and vaporize so as to leave not more than a dark stain (abs. of sugars and dextrin, which leave a porous coal). A portion heated to about 85° C. (185° F.) with test-solution of potassio-cupric tartrate should not give a decided yellowish-brown precipitate, and the same result should be obtained if, before applying this test, another portion be boiled with a little diluted hydrochloric acid for half an hour (abs. of sugars). After full combustion no residue should be left (metallic salts). Diluted with 10 times its volume of distilled water, portions should give no precipitates or colors when treated with test-solution of nitrate of silver, chloride of barium, chloride of calcium, sulphide of ammonium, or oxalate of ammonium (acrylic or hydrochloric, sulphuric, oxalic acid, iron, or calcium salts)."—U. S. P.

Tests.—Heat one or two drops of glycerin in a test-tube, or with strong sulphuric acid, acid sulphate of potassium, or other salt powerfully absorbent of water; vapors of acrolein (from *acer*, sharp, and *oleum*, oil) are evolved, recognized by their powerfully irritating effects on the eyes and respiratory passages. If the glycerin be in solution, it must be evaporated as low as possible before applying this test.—Add a few drops of the fluid suspected to contain glycerin to a little powdered borax; stir well together; dip the looped end of a platinum wire into the mixture and expose to an air-gas flame: a deep green color is produced (Senier and Lowe).

The glycerin liberates boracic acid, and it is the latter which colors the flame. Ammoniacal salts, which similarly affect borax, must first be got rid of by boiling with solution of carbonate of sodium. Liquids containing much indefinite organic matter must sometimes be evaporated to dryness, the residue extracted by alcohol, and the latter tested for the glycerin. To detect traces liquids must be concentrated.

Besides glycerin itself (*Glycerinum*, U. S. P.), solutions or mixtures of starch and of yolk of egg and glycerin (*Glyceritum Amyli*, U. S. P.; *Glyceritum Vitelli*, or *Glyconin*, U. S. P.) are official.

QUESTIONS AND EXERCISES.

796. Give the formulæ of some compounds of radicals which have the general formula $C_nH_{2n-7}{}'$, $C_nH_{2n-1}{}'$, $C_nH_{2n-1}{}'''$, and $C_nH_{2n}{}''$,—*e. g.* benzol, essential oil of mustard, glycerin, and glycol.

797. State the difference in composition of natural and artificial oil of bitter almonds.

798. How is the so-called artificial oil of bitter almonds prepared?

799. What are the uses, composition, source, and properties of Carbolic Acid?

800. State the characters by which carbolic acid is distinguished from Creosote.

801. In what relation does carbolic acid stand to cresylic acid?

802. What is the general formula of sulphocarbolates?

803. Draw out an equation explanatory of the production of aniline.

804. Mention the chief properties of Glycerin.

805. What is the specific gravity of glycerin?

806. By what test is glycerin recognized?

807. Enumerate some official preparations in which glycerin is employed as a solvent.

ALBUMENOID SUBSTANCES.

Albumen.—Agitate thoroughly white of egg (*Albumen Ovi*, B. P.) with water, and strain or pour off the liquid from the flocculent membranous insoluble matter. One white to 100 c.c. of water forms the "Test-Solution of Albumen," U. S. P.

Test.—Heat a portion of this solution of albumen to the boiling-point; the albumen becomes insoluble, separating in clots or coagula of characteristic appearance.

Other Reactions.—Add to small quantities of aqueous solution of albumen solutions of corrosive sublimate, nitrate of silver, sulphate of copper, acetate of lead, alum, perchloride of tin; the various salts not only coagulate, but form insoluble compounds with albumen. Hence the value of an egg as a temporary antidote in cases of poisoning by many metallic salts, its administration retarding the absorption of the poison until the stomach-pump or other measures can be applied. Sulphuric, nitric, and hydrochloric acids precipitate albumen; the coagulum is slowly redissolved by aid of heat, a brown, yellow, or purplish-red color being produced. Neither acetic, tartaric, nor organic acids generally, except gallo-tannic, coagulate albumen. Alkalies prevent the precipitation of albumen.

Yolk or *Yelk of Egg* (*Vitellus*, U. S. P.) contains only 3 per cent. of albumen, the white 12½. The yolk also contains only 30 per cent. of yellow fat and 14 of casein.

Albumen is met with in large quantities in the serum of blood, in smaller quantity in chyle and lymph, and in the brain, kidneys, liver, muscles, and pancreas. It is not a normal constituent of saliva, gastric juice, bile, or mucus, but occurs in those secretions during inflammation. It is found in the urine and fæces only under certain diseased states of the system.

The cause of the coagulation of albumen by heat has not yet been discovered.

Albumen has never been obtained sufficiently pure to admit of its composition being expressed by a trustworthy formula: Gerhardt regarded it as a sodium compound ($HNaC_{72}H_{110}N_{18}SO_{22},H_2O$).

Egg-albumen (and, to some extent, blood-albumen) is largely used by calico-printers as a vehicle for colors, serving also, when dry, as a glaze. Curriers prize egg oil for softening leather.

Albumen coagulated by heat is said to be recoverable in a scarcely altered fluid condition by contact with a dilute aqueous solution of a very small proportion of pepsin.

Fibrin, Casein, Legumin.

Fibrin is the chief constituent of the muscular tissue of animals. It occurs in solution in the blood, and its spontaneous solidification or coagulation is the cause of the *clotting* of blood shortly after being drawn from the body—a phenomenon which cannot at present be explained satisfactorily. Fibrin may be obtained by whipping fresh blood with a bundle of twigs, separating the adherent fibres, and washing in water till colorless. It may be dried or kept under spirit of wine.

Average Composition of Blood (*in 1000 Parts*).
(Compiled by Kirkes).

	Water		784
	Albumen		70
	Fibrin		2.2
	Red corpuscles (dried)		130
Fatty matters.	Cholesterin	0.08	1.4
	Cerebrin	0.40	
	Serolin	0.02	
	Oleic and margaric acids		
	Volatile and odorous fatty acid		
	Fat containing phosphorus		
Inorganic salts.	Chloride of sodium		3.6
	Chloride of potassium		.35
	Phosphate of sodium (Na_3PO_4)		.2
	Carbonate of sodium		.82
	Sulphate of sodium		.28
	Phosphates of calcium and magnesium		.25
	Oxide and phosphate of iron		.50
	Extractive matters, biliary coloring-matter, gases, and accidental substances		6.4
			1000.00

Percentage proportion of the *chief* constituents of Blood.

Water	78.4
Red corpuscles (solid residue)	13.0
Albumen of serum	7.0
Inorganic salts	.603
Extractive, fatty, and other matters	.777
Fibrin	.22
	100.000

Casein occurs in Cow's Milk (*Lac*, B. P.) to the extent of 3 per cent. dissolved by a trace of alkaline salt. Its solution does not spontaneously coagulate like that of fibrin, nor by heat like albumen; but acids cause its precipitation from milk in the form of a curd (cheese) containing the fat-(butter)-globules previously suspended in the milk, a clear yellow liquid (or whey) remaining. *Curds and whey* are also produced on adding to milk a piece or an infusion of *rennet*, the salted and dried inner membrane of the fourth stomach of the calf. The exact action of rennet is not known. Respecting rennet, Soxhlet says: "60 to 80 grains of calf's stomach, steeped for five days in 1 litre of a 5-per cent. solution of common salt at ordinary temperatures, yield a solution of which 1 vol. will coagulate 10,000 vols. of new milk at a temperature of 95° F. in forty minutes. If the filtered solution is treated with 60 to 90 grains more of stomach, a solution of double strength is obtained; another repetition gives a solution three times the strength of the original one. To prevent decomposition, about 0.3 per cent. of thymol may be added to the concentrated rennet extract solution. Possibly a slight taste due to this may be detected in the finest cheese, but for the same reason oil of cloves is much more objectionable. Boracic acid is on all accounts the best antiseptic to employ, and solutions to which it has been added may be kept in covered vessels for months. All extract-solutions lose strength on keeping; during the first two months the solution may become 30 per cent. weaker, then the strength remains nearly constant for eight months in the case of a solution of 1 in 18,000. Alcohol is almost as good an antiseptic as boracic acid if the solution be preserved in well-stoppered flasks."

Average Composition of 1000 Parts of Milk.

	Specific gravity.	Water.	Solid constituents.	Casein and extractive.	Sugar.	Butter.	Salts.
Woman . .	1.030–1.034	870	130	37	50	40	3
Cow	1.030–1.035	877	123	40	46	30	7

Specific gravity alone, as taken by the form of hydrometer termed a *lactometer*, or even by more delicate means, is of little value as an indication of the richness of milk, the butter and the other solids exerting an influence in opposite directions. Good cow's milk affords from 10 to 12 per cent. by volume of cream and 3 to 3½ per cent. of butter. The water of milk seldom varies more than from 87 to 88 per cent., and the solid constituents from 13 to 12. Indeed, excluding its butter, the milk of healthy cows is curiously regular in composition. The non-fatty solids in the mixed milk of a herd or dairy of healthy cows is almost a constant quantity—namely, 9.3 per cent. A lower proportion of non-fatty solids in a sample of milk points to the addition of water. Thus, supposing that 100 grains of a specimen of milk evaporated to dryness, and all butter extracted from the residue by ether, yielded a non-fatty residue of 7.44 grains, the specimen would probably be four-fifths milk and one-fifth water. For if 9.3 indicate 100, then 7.44 indicate 80. Occasionally, under exceptional circumstances, a sample of genuine milk might be slightly poorer than that from a healthy herd, and therefore in England, for legal purposes, a standard of 9 per cent. by weight of non-fatty solids and 2.5 per cent. of butter-fat has been proposed. Only in the rare cases of milk containing an unusually large proportion of butter-fat would any milk yielding less than 9 per cent. of non-fatty solids be regarded as genuine. And, again, no milk would be considered genuine, under this standard, if it yielded less than 2.5 per cent. of fat, not even in the rare case of its containing an unusually large proportion of real non-fatty milk-solids. Half-starved cows might yield milk below these standards, but it could scarcely be considered to be genuine or better fitted for food than milk watered *after* leaving the cow. If, however, such milk is to be regarded as genuine, a standard of 8.5 of non-fatty solids will not be too low.

Under the microscope milk is seen to consist of minute corpuscles floating in a transparent medium. These corpuscles consist of fatty matter (butter), said to be contained in a filmy albumenoid envelope. The fat is fluid at the normal temperature of the animal, and remains so until the milk is well agitated by churning or otherwise, or until the milk is frozen.

Legumin, or *vegetable casein*, is found in most leguminous seeds, such as sweet and bitter almonds. Peas contain about 25 per cent. of legumin.

Vegetable albumen is contained in many plant-juices, and is deposited in flocculi on heating such liquids. *Vegetable fibrin* is the name given by Liebig and Dumas to the portion of the gluten of wheat which is insoluble in alcohol and ether (*vide* p. 401).

Albumenoid substances are nearly identical in percentage composition. Albumen (and fibrin) contains 53.5 of carbon, 7 of hydrogen, 15.5 of nitrogen, 22 of oxygen, 1.6 of sulphur, and .4 of phosphorus. Casein contains no phosphorus. These three bodies are often termed the *plastic elements of nutrition*, under the assumption that animals directly assimilate them in forming muscles, nerves, and other tissues—starch, sugar, and similar matter forming the *respiratory* materials of food, because more immediately concerned in keeping up the temperature of the body by the combustion going on between them and their products and the oxygen of the air in the blood. The whole of the organic nitrogen in food must not, however, be regarded as representing true albumenoids, some existing as amidic and similar compounds—bodies having a simplicity of composition characteristic of the *products* of physiological action on food, rather than that complexity of composition characteristic of true nutrients. Albumenoids in decomposing yield much fatty as well as other substances. Possibly, a portion, at least, of the *adipocire* (*adeps*, fat; *cera*, wax), or *corpse-fat*, characteristic of the remains of buried animals, is thus derived.

Musk (*Moschus*, U. S. P.), "the dried secretion from the preputial follicles of *Moschus moschiferus*" (the Musk Deer), is a mixture of albumenoid, fatty, and other animal matters with a volatile odorous substance of unknown composition.

GELATIGENOUS SUBSTANCES.

These nitrogenous bodies differ chemically from the albumenoid in containing less carbon and sulphur and more nitrogen. They are contained in certain animal tissues, and on boiling with water yield a solution which has the remarkable property of solidifying to a jelly on cooling. The tendons, ligaments, bones, skin, and serous membranes afford *gelatin* proper; the cartilages give *chondrin*, which differs from gelatin in composition and in being precipitated by vegetable acids, alum, and the acetates of lead. The purest variety of gelatin is *isinglass*, B. P. (*Ichthyocolla*, U. S. P.), the swimming-bladder or sound of various species of *Acipenser*, Linn., prepared and cut in fine shreds. Small quantities are more easily disintegrated by a file than a knife. Fifty grains dissolved in

5 ounces of distilled water forms the official "Solution of Gelatin," B. P. *Glue* is an impure variety of gelatin, made from the trimmings of hides; *size* is glue of inferior tenacity, prepared from the parings of parchment and thin skins. "Among the varieties of gelatin derived from different tissues and from the same sources at different ages, much diversity exists as to the firmness and other characters of the solid formed on the cooling of the solutions. The differences between isinglass, size, and glue in these respects are familiarly known, and afford good examples of the varieties called weak and strong, or low and high, gelatin. The differences are sometimes ascribed to the quantities of water combined in each case with the pure or anhydrous gelatin, part of which water seems to be intimately united with the gelatin; for no artificial addition of water to glue would give it the character of size, nor would any abstraction of water from isinglass or size convert it into the hard, dry substance of glue. But such a change is effected in the gradual process of nutrition of the tissues; for, as a general rule, the tissues of an old animal yield a much firmer or stronger jelly than the corresponding parts of a young animal of the same species" (Kirkes's *Physiology*).

Gelatin appears to unite chemically with a portion of the water in which it is soaked when used for culinary and manufacturing purposes, for a solution of glue in a hot anhydrous glycerin does not yield an ordinary jelly on cooling. From its solution in water gelatin is precipitated by alcohol, corrosive sublimate, perchloride of platinum, and by tannic acid. Its aqueous solution is not, like that of albumen, coagulated by heat. By prolonged ebullition its gelatinizing power is destroyed.

PEPSIN.

Pepsin (from πέπτω, *peptō*, I digest) is a nitrogenous substance existing in the gastric juice and as a viscid matter in the *peptic* glands and on the walls of the stomach of animals. To isolate it, the mucous membrane of the stomach (of the hog, sheep, or calf, killed fasting) is scraped, and macerated in cold water for twelve hours; the pepsin in the strained liquid is then precipitated by acetate of lead, the deposit washed once or twice by decantation, sulphuretted hydrogen passed through the mixture of the deposit with a little water to remove the whole of the lead, and the filtered liquid evaporated to dryness at a temperature not exceeding 105° F. Pepsin is a powerful promoter of digestion; its solution is hence frequently termed *artificial gastric juice.* As met with in pharmacy its strength varies greatly. It is often prepared by simply mixing with starch the thick liquid obtained on macerating the scraped stomach with water, and evaporating to dryness. (Vide *Pharmaceutical Journal*, 1865–66, p. 112, and 1871–72, pp. 785 and 843.) The English official process (*Pepsin*, B. P.) simply consists in scraping the viscid pulp from the slightly washed inner surface of the stomach, and quickly evaporating it to dryness on glass or glazed earthenware at a temperature not exceeding 100° F. The product is powdered. "A light yellowish-brown powder, having a faint, but not disagreeable odor, and a slightly saline taste, without any indication of putrescence. Very little soluble in water or spirit. Two grains of it with an ounce of distilled water, to which five minims of hydrochloric acid have been added, form a mixture in which 100 grains of hard-boiled white of egg, in thin shavings (or, better, in pulp formed by passing it through copper wire gauze containing thirty-six meshes to the inch), will dissolve on their being digested together for about four hours at a temperature of 98° F. (or, better, 130° F.). The solvent or digestive action of pepsin on the albumenoids, etc. in the stomach results in a fluid termed *peptone*. It is thus that such food is prepared for conversion into blood. Artificial peptone is made by digesting blood-fibrin with pepsin in very weak hydrochloric acid. Peptone is not readily coagulated by heat, and it freely diffuses through membranes. It appears to be isomeric with albumen. Some vegetables, notably the leaves of the papaw tree, *Carica papaya*, appear to contain a principle, "papaine," analogous in properties to pepsin. According to Wurtz, papaine is an albumenoid.

(For a *résumé* of the different modes of preparing pepsin, see an article by Petit in the *Pharmaceutical Journal* for July 17, 1880.)

The preparation official in the United States is *Pepsinum Saccharatum:* "1 part of Saccharated Pepsin, dissolved in 500 parts of water acidulated with 7.5 parts of hydrochloric acid, should digest at least 50 parts of hard-boiled egg-albumen in five or six hours at a temperature of 38° to 40° C. (100° to 104° F.)."

Liquor Pepsini, U. S. P., is a mixture of 40 parts of saccharated pepsin, 12 of hydrochloric acid, 400 of glycerin, and water to make 1000. It should not develop an ammoniacal odor on keeping (abs. of mucus).

PANCREATIN.

The pancreas (or "sweetbread") secretes a colorless fluid which contains 1½ to 2½ per cent. of an albumenoid substance which has the power of converting starch into sugar, and, especially, of emulsifying fat. It may be precipitated by chloride of sodium from an acidulated infusion of the pancreas. It is soluble in cold water. An extremely small proportion emulsifies a large volume of fat.

QUESTIONS AND EXERCISES.

808. In what form is albumen familiar?

809. Name the chief test for albumen.

810. Why is the administration of albumen useful in cases of poisoning?

811. Mention the points of difference between yolk and white of egg.

812. From what source other than egg may albumen be obtained?

813. In what respect does fibrin differ from albumen?

814. Enumerate the chief constituents of blood?
815. How may fibrin be obtained from blood?
816. State the difference between casein, fibrin, and albumen.
817. What are the relations of cream, butter, curds and whey, and cheese, to milk?
818. Describe the microscopic appearance of blood and of milk.
819. How much cream should be obtained from good milk?
820. What is the percentage of water in genuine milk?
821. Name sources of vegetable casein and vegetable albumen.
822. Give the percentage of nitrogen in albumenoid substances.
823. Describe the chemical nature of Musk.
824. In what lie the peculiarities of Gelatin?
825. To what extent do isinglass, glue, and size differ?
826. Whence is Pepsin obtained?
827. How is pepsin prepared?

FATTY BODIES.

SOAPS, SOLID FATS, FIXED OILS, VOLATILE OILS, CAMPHORS.

General Relations.—Oils and fats are, apparently, almost as simple in constitution as ordinary inorganic salts. Just as acetate of potassium ($KC_2H_3O_2$) is regarded as a compound of potassium (K) with the characteristic elements of all acetates ($C_2H_3O_2$), so soft soap is considered to be a compound of potassium (K) with the elements characteristic of all oleates ($K_{18}H_{33}O_2$), and hence is chemically termed oleate of potassium ($KC_{18}H_{33}O_2$). Olive oil, from which soap is commonly prepared, is mainly oleate of the trivalent radical *glyceryl* (C_3H_5), the formula of pure fluid oil being $C_3H_5 3C_{18}H_{33}O_2$, and its name *olein*. The formation of a soap, therefore, on bringing together oil and a moist oxide or hydrate, is a simple case of double decomposition, or, rather, metathesis, as seen already in connection with lead plaster (p. 209), or in the following equation relating to the formation of common hard soap:—

$3NaHO$	$+$	$C_3H_5 3C_{18}H_{33}O_2$	$=$	$3NaC_{18}H_{33}O_2$	$+$	$C_3H_5 3HO$
Hydrate of sodium (caustic soda).		Oleate of glyceryl (vegetable oil).		Oleate of sodium (hard soap).		Hydrate of glyceryl (glycerin).

Berthelot has succeeded in preparing oil artificially from oleic acid and glycerin, and it is said to be identical with the pure olein of olive and of other fixed oils. Hard fats chiefly consist of *stearin*—that is, of tristearate of glyceryl ($C_3H_5 3C_{18}H_{35}O_2$). Mr. Wilson, of Price's Candle Company, obtains stearic and oleic acids and glycerin by simply passing steam, heated to 500° or 600° F., through melted fat. Both the glycerin and fat acids distil over in the current of steam, the glycerin dissolving in the condensed water, the fat-acids floating on the aqueous liquid.

Oleic acid (*Acidum Oleicum*, U. S. P.), when quite pure, is a light-yellow, almost inodorous, and tasteless oil, of sp. gr. 0.800 to 0.810. At low temperatures it thickens, and when near the freezing-point of water crystallizes. The occurrence of any important quantity of palmitic acid or stearic acid may be proved by saponifying with carbonate of potassium, neutralizing the product with acetic acid, precipitating with acetate of lead, washing the lead oleate with a little hot water, and adding ether: the oleate will dissolve the palmitate, and stearate of lead be insoluble. Any fixed oil will float on the surface when equal volumes of the oleic acid and of alcohol are warmed to 25° C.

The author found (*Pharmaceutical Journal*, March, 1863) that oleic acid readily combines with alkaloids and most of the metallic oxides or hydrates, forming oleates which are soluble in fats. In this way active medicines may be administered internally in conjunction with oils or externally in the form of ointments. (*Oleatum Hydrargyri*, U. S. P.; *Oleatum Veratrinæ*, U. S. P.)

As regards the conversion of oily substances into emulsions resembling the common natural emulsion milk, Gregory states that 3 drachms of gum-acacia in fine powder are necessary to emulsify 1 ounce of any of the volatile oils, and that a little less (about 2 drachms) will answer for the fixed oils and balsams. To this quantity of gum 4½ drachms of water must be added (no more and no less). Either the water or the oil may be added first to the gum, but it is quickest to add the oil first, and well triturate before adding the water.

SOAPS.—Olive oil boiled with solution of potash yields potassium soap, or *soft soap* (*Sapo Mollis*, B. P.; *Sapo Viridis*, U. S. P., or *Green Soap*); with soda, sodium soap, or *hard soap* (*Sapo*, U. S. P.); mixed with ammonia, an ammonium soap (*Linimentum Ammoniæ*, U. S. P. with cotton-seed oil); and with lime-water, calcium soap (*Linimentum Calcis*, U. S. P., with cotton-seed oil).—all oleates, chiefly of the respective basylous radicals. Their mode of formation is indicated in the foregoing equation. The alkali soaps are soluble in alcohol, the others insoluble. A green soap, much used on the continent of Europe, and indeed official in Germany (formerly as *Sapo Viridis*, now as *Sapo Kalinus Venalis*), is made by adding indigo to ordinary soft soap, the yellow color of the soap yielding with the indigo a greenish compound. The official characters of Hard Soap are: "Grayish-white, dry, inodorous; horny and pulverizable when kept in dry warm air; easily moulded when heated; soluble in rectified spirit, leaving not more than 3 per cent. of insoluble matter, of which at least two-thirds are soluble in water. A 4-per cent. alcoholic solution should not gelatinize on cooling (abs. of animal fats), not imparting an oily stain to paper; incinerated, it yields an ash which does not deliquesce." And of Soft Soap: "Yellowish-green, inodorous, of a gelatinous consistence; soluble in rectified spirit; not imparting an oily stain to paper; when dried yielding nothing to benzol; incinerated, it yields an ash which is very deliquescent." Curd Soap (*Sapo Animalis*, B. P.) is a "soap made with soda and a purified animal fat, consisting principally of stearin." It will, of course, chiefly contain stearate of sodium. In pharmacy it is often advantageously employed instead of the "hard soap." *Castile* and *Marseilles* soaps are sodium soaps "mottled" by iron soap.

The hard soap met with in trade is made from all varieties of oil, the commoner kinds being simply the product of the evaporated mixture of oil and alkali, while the better sorts have been separated from alkaline impurities, and the glycerin by the addition of common salt to the liquors, which causes the precipitation of the pure soap as a curd. Potash soap is not precipitable by salt.

Bile (*Fel Bovis*, U. S. P.) is, officially, the gall of the ox (*Bos taurus*, Linn.), either heated to 80° C., strained, and evaporated from 100 parts to 15 (*Fel Bovis Inspissatum*, U. S. P.), or freed from mucus by agitating with alcohol (in which mucus is insoluble), filtering, and evaporating. The latter is the official Purified Ox-Bile (*Fel Bovis Purificatum*, U. S. P.); it has a resinous appearance, but is chiefly composed of two crystalline substances having the constitution of a soap; the one is termed *taurocholate of sodium* ($NaC_{26}H_{42}NO_6S$), the other is *glycocholate*, or simply *cholate of sodium* ($NaC_{26}H_{44}NO_7S$). Both taurocholates and glycocholates are conjugated bodies readily yielding, the former *cholic* or *cholalic acid* ($HC_{24}H_{39}O_5$) and *taurine* ($C_2H_7NO_3S$), the latter cholalic acid and *glycocine* or *glycocoll* ($C_2H_5NO_2$), a soluble crystalline body having interesting physiological relations, inasmuch as it is obtainable from gelatin (hence the name glycocoll or sugar of gelatin, from γλυχὺς, *glucūs*, sweet, and κόλλα, *kolla*, glue) and from hippuric acid. The presence of bile in a liquid, such as urine, may be detected by the following tests: The fluid is gradually mixed with half its bulk of strong sulphuric acid in a test-tube, rise of temperature being prevented by partial immersion of the tube in water. A small quantity of powdered white sugar is then introduced and well mixed with the acid liquid, and more sulphuric acid then poured in; as the temperature rises a reddish or violet coloration is produced. The cholacic acid liberated in the reaction furnishes the color. This is Pettenkofer's test. It is somewhat interfered with by albumen and by volatile oils. Quinlan tests for bile by placing a three-millimetre stratum of the suspected fluid before the slit of a spectroscope and observing the absorption, which extends, according to the amount present, from the violet of the spectrum as far as the Fraunhöfer line D.

SOLID FATS.—1. *Lard* (*Adeps*, U. S. P.) is the purified internal fat of the abdomen of the hog—the perfectly fresh *omentum* or *flare*, washed, melted, strained, and dried. *Lard Oil* (*Oleum Adipis*, U. S. P.), which is chiefly olein, is "a fixed oil expressed from lard at a low temperature." Sp. gr. 0.900 to 0.920. 2. *Benzoated Lard* (*Adeps Benzoinatus*, U. S. P.) is lard heated over a water-bath with

2 per cent of benzoin, which communicates an agreeable odor and prevents or retards rancidity. Lard is a mixture of olein and stearin; *margarin*, the margarate of glyceryl, was formerly supposed to be a constituent of lard and other soft fats, but is now regarded as a mere mixture of *palmitin* (the chief fat of palm oil) and stearin. 3. *Yellow Wax* (*Cera Flava*, U. S. P.), (sp. gr. 0.955 to 0.967; melting-point 63° to 64° C.), the prepared honeycomb of the Hive-Bee, and the same bleached by exposure to sunlight. 4. *White Wax* (*Cera Alba*, U. S. P.) (sp. gr. 0.965 to 0.975; melting-point about 65° C.), according to Brodie, is chiefly a mixture of *Cerotic Acid* ($HC_{27}H_{53}O_2$), *Palmitate of Melissyl* ($C_{30}H_{61}C_{16}H_{31}O_2$), and about 5 per cent. of *Ceroleine*, the body to which the color, odor, and tenacity of wax are due. "If 1 gm. of yellow wax be boiled, for half an hour, with 40 gm. of solution of soda (sp. gr. 1.180), the volume being preserved by the occasional addition of water, the wax should separate on cooling, without rendering the liquid opaque, and no precipitate should be produced in the filtered liquid by hydrochloric acid (abs. of fats or fatty acids, Japan wax, resin); nor should the same reagent produce a precipitate in water which has been boiled with a portion of the wax (abs. of soap). If 5 gm. of wax be heated in a flask for fifteen minutes with 25 gm. of sulphuric acid to 160° C. (320° F.), and the mixture diluted with water, no solid, wax-like body should separate (abs. of paraffin)."—U. S. P. *Cerecine*, the purified native *ozokerita* (*ὄζω*, *ozō*, I smell; *χηρός*, *keros*, wax) of Galicia, is a solid hydrocarbon largely used as a substitute for beeswax, especially in Russia. It differs from beeswax chemically in being almost unattacked by warm oil of vitriol. 5. *Spermaceti* (*Cetaceum*, U. S. P.) is the *palmitate of cethyl* ($C_{16}H_{33}C_{16}H_{31}O_2$), or *cetine;* when saponified it yields, not glycerin, the hydrate of glyceryl (C_3H_53HO), but *ethal*, the hydrate of cetyl ($C_{16}H_{33}HO$); it is the solid crystalline fat accompanying *sperm* oil in the head of the spermaceti whale. Sp. gr. about 0.945; melting-point near 50° C. 6. *Suet*, the internal fat of the abdomen of the sheep, purified by melting and straining, forms the official *Sevum*, U. S. P.; it is almost exclusively composed of stearin ($C_3H_53C_{18}H_{35}O_2$). 7. Expressed oil of *nutmeg* (*Oleum Myristicæ Expressum*, B. P.), commonly but erroneously termed *Oil of Mace*, is a mixture of a little volatile oil with much yellow and white fat; the latter is *myristin* or myristate of glyceryl ($C_3H_53C_{14}H_{27}O_2$). 8. Oil of *theobroma*, or *Cacao-butter* (*Oleum Theobromæ*, U. S. P.), chiefly theobromate of glyceryl (Kingzett), is a solid product of the roasted and roughly crushed seeds or *cocoa-nibs* of the *Theobroma cacao*. They contain from one-fourth to one-half of this fat; melting-point 15° C. These also furnish, when ground, *flake cocoa;* or when ground and much sweetened, *chocolate;* or with farina and some sugar, *cocoa;* or with a portion of the butter extracted, "cocoatina," etc. 9. *Cocoa-nut* oil or butter, a soft fat largely contained in the edible portion of the nut of *Cocos nucifera*, or common cocoa-nut of the shops, a body containing glyceryl united with no less than six different univalent acidulous radicals—namely, the caproic ($C_6H_{11}O_2$), caprylic ($C_8H_{15}O_2$), rutic ($C_{10}H_{19}O_2$), lauric ($C_{12}H_{23}O_2$), myristic ($C_{14}H_{27}O_2$), and palmitic

($C_{16}H_{31}O_2$), radicals which, like some from common resin, when united with sodium, form a soap differing from ordinary hard soap (oleate of sodium) by being tolerably soluble in a solution of chloride of sodium; hence the use of cocoa-nut oil and resin in making *marine soap*, a soap which, for the reason just indicated, readily yields a lather in sea-water. 10. *Kokum Butter*, Garcinia Oil, or Concrete Oil of Mangosteen, a whitish or yellowish-white fat obtained from the seeds of *Garcinia indica* or *G. purpurea*, is composed of stearin, myristicin, and olein. It is recognized officially in the Pharmacopœia of India (*Garciniæ Purpureæ Oleum*).

Butter yields 87½ per cent. of fat acids by saponification and decomposition of the soap by acid. Other animal fats, with which butter is likely to be adulterated, yield 95½. Hence the percentage of fat acid yielded by a suspected sample of butter indicates not only purity or the opposite, but the extent of sophistication.

FIXED OILS.—*Fixed* and *Volatile* oils are naturally distinguished by their behavior when heated; they also differ generally in chemical constitution, a fixed oil being, apparently, a combination of a basylous with an acidulous radical, while a volatile oil is more commonly a neutral hydrocarbon or the same oxidized.

Drying and Non-drying Oils.—Among fixed oils, most of which are oleate with a little palmitate and stearate of glyceryl, a few, such—as (1) *Linseed oil* (*Oleum Lini*, U. S. P., contained in *Linum*, U. S. P., *Linseed* or *Flaxseed*, the ground residue of which "should yield, when extracted with disulphide of carbon, not less than 25 per cent. of fixed oil," is *linseed meal*), and (2) *Cod-liver oil* (*Oleum Morrhuæ*, U. S. P.), and to some extent *castor* and *croton*—are known as *drying oils*, from the readiness with which they absorb oxygen and become hardened to a resin. Linseed commonly contains 37 or 38 per cent. of oil; 25 to 27 per cent. is obtained by submitting the ground seeds to hydraulic pressure, 10 or 12 per cent. remaining in the residual *oil cake*. *Boiled oil* is linseed oil which has been boiled with oxide of lead. This treatment increases the already great tendency of linseed oil to resinify, forming *linoxyn*, $C_{32}H_{54}O_{11}$, on exposure to air. The drying oils appear to contain linolein, an oily body distinct from olein. Cod-liver oil contains a trace of iodine. Among the *non-drying oils* are the following: (3) *Almond* oil (*Oleum Amygdalæ Expressum*, U. S. P.), indifferently yielded by the bitter (*Amygdala Amara*, U. S. P.) or sweet seed (*Amygdala Dulcis*, U. S. P.) to the extent of 45 and 50 per cent. respectively. (3*a*) *Cotton-seed* oil (*Oleum Gossypii Seminis*, U. S. P.) contains olein and some palmitin. Sp. gr. 0.920 to 0.930. It should not be permanently colored dirty yellow by sulphuric acid. (4) *Croton* oil (*Oleum Crotonis*, B. P., and *Oleum Tiglii*, U. S. P.). Geuther states that no such acid as crotonic is obtainable from croton oil, but acetic, butyric, valerianic, and higher members of the oleic series, together with *tiglic acid*, $HC_5H_7O_2$. (5) *Lycopodium* (U. S. P.), a yellow powder composed of the spores of the common Club-Moss (*Lycopodium clavatum*), contains a large proportion of a very fluid fixed oil; also an alkaloid (Bödeker), $C_{32}H_{52}N_2O_3$. (6) *Olive* oil (*Oleum Olivæ*, U. S. P.), already noticed (p. 462). "If 1 gm. of olive oil be agitated in a test-tube with 2 gm. of a cold mixture prepared from equal volumes of strong sulphuric acid and of nitric acid of sp. gr. 1.185, and the mixture be set aside for half an hour, the supernatant oily layer should not have a darker tint than yellowish; nor should a green or red layer separate on standing if 1 gm. of the oil be shaken for a few seconds with 1 gm. of a cold mixture of sulphuric acid (sp. gr. 1.830) and nitric acid (sp. gr. 1.250), and 1 gm. of disulphide of carbon; and if 5 drops of the oil are let fall upon a thin layer of sulphuric acid in a flat-bottomed capsule, no brown-red or dark-brown zone should be developed within three minutes at the line of contact of the two liquids (abs. of appreciable quantities of other fixed oils of similar physical properties)."—U. S. P. (7) *Castor* oil (*Oleum Ricini*, U. S. P.), chiefly a *ricinoleate of glyceryl* ($C_3H_53C_{18}H_{33}O_3$) or ricinolein, a slightly oxidized olein, soluble, unlike most fixed oils, in alcohol and in glacial acetic acid. Castor-oil seeds are stated, by Tuson, to contain an alkaloid, *ricinine*. It possesses no purgative property. (8) Oil of *Male Fern*, a vermifuge obtained by exhausting the rhizome (*Aspidium*, U. S. P.) with ether and removing the ether by evaporation—a dark-colored oil containing a little volatile oil and some resin, and officially termed an oleoresin (*Oleoresina Aspidii*, U. S. P.). Its chief active constituent appears to be *filicic acid*, $C_{14}H_{18}O_5$. (9) Fixed oil of *Mustard*, a bland, inodorous, yellow or amber oil, yielding, by saponification and action of sulphuric acid, glycerin, oleic acid, and *erucic acid* ($HC_{22}H_{41}O_2$) (Darby). (10) *Arachis* oil (*Oleum Arachis*, P. I.) is found to the extent of 40 or 50 per cent. in the seeds of *Arachis hypogæa* (P. I.), the Ground-nut or Earth-nut (so called because the pod of the herb in the growth of its stalk downward is forced beneath the surface of the ground, and there ripens). It is chiefly olein, but contains hypogæin, palmitin, and arachin. The oil is largely used in India in the place of olive oil, and is becoming much employed in Europe, especially for soap-making. (11) *Sesame* oil, or oil of *sesamum* (*Oleum Sesami*, U. S. P.) (Gingelly, Teal, or Benné Oil), from the seeds of *Sesamum indicum*, is also largely used in Europe. It has most of the characters of the best olive oil. (12) *Shark-liver oil*, from *Squalus carcharis* (*Oleum Squalæ*, P. I.), is used to some extent as a substitute for cod-liver oil in India.

Their physical qualities and the formulæ of their acidulous radicals show that the fatty bodies are closely related, and indicate that the natural processes by which they are formed are probably as closely related. The following Table shows the homology of the fat-acids, and gives their names, formulæ, melting-points, boiling-points, and natural and artificial sources. (For further information respecting these acids and their isomers, the reader is referred to the Index, to works on Organic Chemistry, to larger chemical works, or to Watt's *Dictionary of Chemistry*.)

Acids.	Formulæ. Molec. Vol. = 2.	Melting-point.		Boiling-point.		Whence obtained.	
		° F.	° C.	° F.	° C.		
Formic.......	$HC\ H\ O_2$	47.3	8.5	212	100	Red ants; distillation of oxalic acid: and oxidation of amylaceous and other organic bodies.	
Acetic........	$HC_2\ H_3\ O_2$	62	16.7	244.4	118	Distillation of wood: oxidation of alcohol, etc.	By oxidation of oleic with nitric acid.
Propionic...	$HC_3\ H_5\ O_2$	– 5.8	– 21	285.2	140.7	Fermentation of glycerin, etc.	
Butyric......	$HC_4\ H_7\ O_2$	32	0	324	162.4	Butter: fermentation of lactic acid, etc.	
Valerianic...	$HC_5\ H_9\ O_2$	3.2	– 16	365	185	Valerian root: oxidation of fusel oil.	
Caproic......	$HC_6\ H_{11}O_2$	28.4	– 2	401	205	Butter.	
Œnanthylic.	$HC_7\ H_{13}O_2$	19	– 10.5	435	224	Castor oil by distillation, etc.	
Caprylic.....	$HC_8\ H_{15}O_2$	61.7	– 16.5	457	236	Butter: cocoa-nut oil.	
Pelargonic..	$HC_9\ H_{17}O_2$	54.5	12.5	489	254	Leaves of the geranium.	
Rutic.........	$HC_{10}H_{19}O_2$	86	30	516	269	Butter; oil of rue by oxidation.	
Lauric........	$HC_{12}H_{23}O_2$	110	43	....	....	Cocoa-nut oil: berries of the bay tree.	
Myristic.....	$HC_{14}H_{27}O_2$	129	54	....	....	Nutmeg-butter; cocoa-nut oil, etc.	
Palmitic.....	$HC_{16}H_{31}O_2$	143.6	62	....	....	Palm oil; butter; beeswax, etc.	
Stearic.......	$HC_{18}H_{35}O_2$	159	70.5	....	....	Most solid animal fats.	
Arachidic...	$HC_{20}H_{39}O_2$	167	75	....	....	Butter; oil of ground-nut.	
Cerotic.......	$HC_{27}H_{53}O_2$	174	79	....	....	Beeswax.	
Melissic......	$HC_{30}H_{59}O_2$	192	89	....	....	Beeswax.	

QUESTIONS AND EXERCISES.

828. Give a sketch of the general chemistry of fixed oils, fats, and soaps.

829. What is the difference between hard and soft soap?

830. Which soaps are official?

831. Name the source of lard, and state how "Prepared Lard" is obtained.

832. State the composition of Beeswax.

833. In what does Spermaceti differ from other solid fats?

834. Mention the chief constituent of Suet?

835. Whence is Cacao-Butter obtained?

836. Why is *marine soap* so called, and from what fatty matter is it almost exclusively obtained?

837. What do you understand by *drying* and *non-drying* oils?

838. In what respect does Castor Oil differ from other oils?

839. How is oil of male fern (*Ex. Filicis Liquidum*) prepared?

840. Mention the sources and formulæ of the following fat-acids:

formic, acetic, propionic, butyric, valerianic, caproic, œnanthylic, caprylic, pelargonic, and rutic.

VOLATILE OILS.—The *Volatile* or *Essential Oils* exist in various parts of plants, at first, probably, as mere combinations of carbon and hydrogen; but such *hydrocarbons* are prone to change when in contact with oxygen or moisture; hence these liquids, even when freshly obtained from the plants, and more especially as they occur in pharmacy, are usually mixtures of the liquid hydrocarbons or *elæoptens* (from ἔλαιον, *elaion*, oil, and ὄπτομαι, *optomai*, to see) (pp. 469 to 475) with oxidized hydrocarbons, which are commonly solid or camphor-like bodies termed *stearoptens* (from στέαρ, *stear*, suet) (p. 475). The oils are also often associated with further oxidized bodies termed *resins* (p. 477). Of the hydrocarbons, those most commonly occurring are identical with or are isomers of that from oil of turpentine, and are known as *terpenes*. Tilden separates these terpenes into two groups: a *turpentine group* of true terpenes ($C_{10}H_{16}$), whose members boil at 156° C. to 160° C., yield a nitroso-derivative melting at 129° C., and form a solid crystalline hydrous terpene ($C_{10}H_{20}O_2,H_2O$); and an *orange group* ($C_{15}H_{24}$), polymerides of the true terpenes, whose members boil at 174° C. to 176° C., yield a nitroso-derivative melting at 71° C., and form no solid hydrous compound. Kingzett's researches had previously pointed to a similar grouping, for he showed that turpentine and the other similar hydrocarbons ($C_{10}H_{16}$), and *cymene* ($C_{10}H_{14}$)—the probable nucleus of the terpenes—when mixed with water and subjected to a current of air, yielded to the water peroxide of hydrogen (not ozone), camphor, and camphoric acid, the peroxide of hydrogen and camphoric acid possibly resulting from the action of water on a camphoric peroxide ($C_{10}H_{14}O_4$); while the second class ($C_{15}H_{24}$) yield no peroxide of hydrogen. The members of the $C_{10}H_{16}$ group are easily convertible into their polymers $C_{15}H_{24}$ and $C_{20}H_{32}$ by the action of heat, strong acids, etc. As regards either class, the members often differ from each other in their action on polarized light. Among the oxidized hydrocarbons occur several *aromatic aldehyds;* these, like ordinary aldehyds, form stable crystalline compounds with acid sulphite of sodium. On cooling a volatile oil, a stearopten often crystallizes out, or on distilling an oil it remains in the retort, being less volatile than an elæopten. Volatile oils should obviously be preserved in well-closed bottles. Oxidation also proceeds more slowly in a cold than in a warm temperature.

(For a paper by Symes on the varying power of a large number of essential oils to twist a ray of plane polarized light, see the *Pharmaceutical Journal* for September 13, 1879.)

The process by which volatile oils are usually obtained from herbs, flowers, fruit, or seeds may be imitated on the small scale by placing the material (bruised cloves or caraways, for instance) in a tubulated retort, adapting the retort to a Liebig's condenser, and passing steam, generated in a Florence flask, through a glass tube to the bottom of the warmed retort. The steam in its passage through the substance will carry the oil over the neck of the retort into the condenser, and thence, liquefied and cooled, into the receiving vessel, where the particles of the oil will be found floating on the water. It may be collected by running off the distillate through a glass funnel having a stopcock in the neck, or by letting the water from the condenser drop into an old test-tube which has a small hole in the bottom, or any similar tube placed in a larger vessel, the water and oil being subsequently run off separately from the tube as from a pipette. Volatile oils, like fixed oils, stain paper, but the stain of the former is not permanent like that of the latter. Oils of lemon and orange are sometimes obtained by mere pressure of the rind of the fruit.

The following official (U. S. P.) waters are made by distributing 2 parts of volatile oil over the large surface afforded by four parts of cotton, and percolating with 1000 parts of distilled water: *Aquæ Anisi*, *Cinnamomi*, *Fœniculi*, *Menthæ Piperitæ*, *Menthæ Viridis*. *Aqua Aurantii Florum*, U. S. P., and *Aqua Rosæ*, U. S. P., are obtained by distilling 40 parts of flowers with 200 of water.

The presence of alcohol in an essential oil may be detected and its quantity estimated by shaking with an equal bulk of pure glycerin. The latter dissolves the alcohol, and is augmented in volume according to the amount of alcohol present (Boettger). For tests for the alcohol see page 429.

A large number of volatile oils are employed in medicine, either in the pure state, in the form of saturated aqueous solution (medicated waters), solution of spirit of wine, 1 in 5 (*Essentia Anisi* and *Essentia Menthæ Piperitæ*, B. P.) and 1 in 50 (*Spiritus Cajaputi*, *Juniperi*, *Lavandulæ*, *Menthæ Piperitæ*, *Myristicæ*, *Rosmarini*—B. P.), or as leading constituents in various barks, roots, leaves, etc. The strength of *Spiritus Anisi*, U. S. P., and *Sp. Cinnamomi*, U. S. P., is 10 of oil to 90 of alcohol. *Sp. Menthæ Piperitæ*, U. S. P., and *Sp. Menth. Viridis*, U. S. P., are of similar strength, but also contain whatever may be extracted by the 100 parts of the spirit from 1 part of the dried herb. *Spiritus Aurantii*, U. S. P., contains 6 of oil and 94 of alcohol; *Sp. Gaultheriæ*, U. S. P., *Sp. Juniperi*, U. S. P., *Sp. Lavandulæ*, U. S. P., and *Sp. Myristicæ*, U. S. P., contain 3 of oil and 97 of alcohol; *Spiritus Limonis*, U. S. P., is made with 6 of oil, 4 of freshly-grated lemon-peel, and alcohol sufficient to produce 100 of filtered product. *Perfumes* ("scents" or "essences," including "Lavender-Water" and "Eau de Cologne," or "Cologne-Water, Perfumed Spirit or *Spiritus Odoratus*," as it is termed in U. S. P.) are for the most part solutions of essential oils in spirit of wine or spirituous infusions of materials containing essential oils. The following oils are, directly or indirectly, official in the Pharmacopœias:

1. Volatile oil of *Bitter Almond* (p. 416). 2. Oil of the fruits of *Ajwain* or *Omum*, *Carum Ajowan*, or *Ptychotis Ajowan* (*Fructus Ptychotis*, P. I.), contains *cymol* or *cymene* ($C_{10}H_{11}$) and a stearopten (*Ajwain-ka-phul*, flowers of ajwain) identical with *thymol*, $C_{10}H_{14}O$. 3. Oil of *Dill* (*Oleum Anethi*, B. P.), a pale, yellow, pungent, acrid liquid distilled from dill-fruit; it contains a hydrocarbon, *anethene* ($C_{10}H_{16}$), and an oxidized oil ($C_{10}H_{11}O$) identical with the carvol of oil of caraway (Gladstone). 4. Oil of *Aniseed* (*Oleum Anisi*, U. S. P.), a colorless or pale-yellow liquid, sp. gr. 0.976 to 0.990, of sweetish warm flavor, distilled in Europe from the Anise-fruit (*Pimpinella anisum*) (*Anisum*, U. S. P.), and in China from the fruit of Star-Anise (*Illicium anisatum*) (*Illicium*, U. S. P.); it is a mixture of a hydrocarbon isomeric with oil of turpentine and *anethol*, a stearopten ($C_{10}H_{12}$) which crystallizes out at low temperatures. 5. Oil of *Chamomile* (*Oleum Anthemidis*, B. P.), a bluish, or, when old, yellow oil, of characteristic odor and taste, distilled from chamomile flower-heads (*Anthemis*, U. S. P.). The official variety (*Anthemis nobilis*) yields about 0.2 per cent. of an oil composed of a hydrocarbon ($C_{10}H_{16}$) and an oxidized portion ($C_{10}H_{16}O_2$), which, heated with potash, gives *angelate of potassium* ($KC_5H_7O_2$), whence is obtained *angelic acid* ($HC_5H_7O_2$). According to Demarcay, Kopp, and Köbig, the oil is a mixture of the angelates of butyl and amyl and similar bodies. The flower-heads of another variety, *Matricaria chamomilla* (*Matricaria*, U. S. P.), contain a stearopten ($C_{10}H_{16}O$) having the composition of laurel-camphor. 6. Oil of *Horseradish-root* (*Armoraciæ Radix*, B. P.) is, according to Hofmann, the sulphocyanate of butyl or tetryl (C_4H_9CNS); it is the chief active ingredient of *Spiritus Armoraciæ Compositus*, B. P. 7. Oil of *Sweet-Orange* peel (*Aurantii Dulcis Cortex*, U. S. P.) and Oil of *Bitter-Orange* rind (*Aurantii Amari Cortex*, B. P.; *Oleum Aurantii Corticis*, U. S. P.), the former the flavoring constituent of the official syrup of the *peel* (*Syrupus Aurantii*, U. S. P.), and the oils of various species of *Citrus*--namely, 8, *lemon* (*Oleum Limonis*, U. S. P.), from Lemon Peel (*Limonis Cortex*, U. S. P.); 9, *lime;* 10, *bergamot* (*Oleum Bergamii*, U. S. P.); 11, *citron*, and a variety of citron termed *cedra*—resemble each other in composition, all containing *hesperidene*, a hydrocarbon ($C_{15}H_{24}$), and a small quantity of oxidized hydrocarbons ($C_{10}H_{10}O_5$,$C_{15}H_{10}O$), and (Wright and Piesse) ($C_{20}H_{30}O_3$). Tilden states that lemon oil, distilled from the fresh peel, consists chiefly of a terpene ($C_{10}H_{16}$), boiling at 176° C., with small quantities of a terpene boiling below 160° and a hydrous terpene; the odor of the oil being due to the mixture. Expressed lime-essence also contains a soft resin. 12. *Oleum Aurantii Florum*, U. S. P., Oil of *Neroli*, or *Orange-Flower* (*Aurantii Flores*, U. S. P.), the aqueous solution of which is official in the forms of water (*Aqua Aurantii Florum*, U. S. P.) and syrup (*Syrupus Aurantii Florum*, B. P. and U. S. P.), contains a fragrant hydrocarbon ($C_{10}H_{16}$), colorless when fresh, but becoming red on exposure to light, and an inodorous oxidized hydrocarbon. Strong acids, especially nitric, attack the oil in orange-flower water, coloring the fluid of a rose-tint. 13. Oil of *Petit Grain*, distilled from the leaves and shoots of the orange tree, con-

sists chiefly of a hydrocarbon apparently identical with that of oil of neroli. 14. The leaves of *Boldo* (*Peumus boldus*), a Chilian shrub (tonic and hepatic), yield 2 per cent. of essential oil (and, according to Bourgon and Verne, an alkaloid, *boldine*). 15. Oil of *Buchu-leaves* (*Buchu*, U. S. P.) consists chiefly of a fluid oil ($C_{10}H_{18}O$) holding in solution a crystalline stearopten, *diosphenol* ($C_{14}H_{22}O_3$) (Flückiger). 16. Oil of *Cannabis Indica* (see p. 478). 17. Oil of (the lesser) *Cardamom*, from seeds of the capsules (*Cardamomum*, U. S. P.), is chiefly a hydrocarbon ($C_{10}H_{16}$) isomeric with oil of turpentine and a camphor resembling turpentine-camphor ($C_{10}H_{16}3H_2O$). 18. Oil of *Cajuput* (*Oleum Cajuputi*, U. S. P.) is a mobile bluish liquid, consisting chiefly of *hydrous cajuputene* or *cajuputol* ($C_{10}H_{16},H_2O$). The latter, repeatedly distilled from phosphoric anhydride, yields cajuputene itself ($C_{10}H_{16}$), which has the odor of hyacinths. Fresh cajuput oil has a green hue, which is perhaps transient, for the color of the oil of trade is due to copper (Guibourt and Histed); certainly the green coloring-matter of pure cajuput oil is organic. 19. Oil of *Caraway*-fruit (*Carum*, U. S. P.) (*Oleum Carui*, B. P.; *Oleum Cari*, U. S. P.) is a mixture of *carvene* ($C_{15}H_{24}$) and *carvol* ($C_{10}H_{14}O$). 20. Oil of *Cloves* (*Caryophyllus*, U. S. P.; *Oleum Caryophylli*, U. S. P.) and of *Pimento* or *Pimenta*, U. S. P., or *Allspice* (*Oleum Pimentæ*, U. S. P.), both heavier than water, contain a liquid hydrocarbon ($C_{15}H_{24}$), *eugenic acid* ($C_{10}H_{12}O_2$), a solid body, *eugenin*, isomeric with the eugenic acid, a second crystalline substance, *caryophyllin* ($C_{10}H_{16}O$), isomeric with common camphor, and a salicylic compound. 21. Oil of *Cascarilla-bark* (*Cascarilla*, U. S. P.) has not been fully examined. 22. Oil of *Cinnamon-bark* (*Cinnamomum*, U. S. P.) and of *Cassia-bark* is mostly hydride of cinnamyl or cinnamic aldehyd (C_9H_7OH). Boiled with nitric acid, it furnishes hydride of benzoyl (C_7H_5OH) and benzoic acid ($HC_7H_5O_2$), with chloride of lime yields benzoate of calcium ($Ca2C_7H_5O_2$), and with caustic potash gives cinnamate of potassium ($KC_9H_7O_2$). The specific gravity of oil of Ceylon cinnamon is about 1.040, and of Chinese cinnamon (oil of Cassia) about 1.060. Both are termed *Oleum Cinnamomi* in U. S. P. 23. Oil of *Citronella*, a grass oil, from *Andropogon nardus*, is chiefly composed of *citronellol* ($C_{10}H_{16}O$ and $C_{10}H_{18}O$, Wright), probably isomeric with the *absinthol* from the *Artemisiæ absinthium* or wormwood (*Absinthium*, U. S. P.) (Gladstone). 24. Oil of *Copaiva* or *Copaiba* (*Oleum Copaibæ*, U. S. P.) and, 25, of *Cubebs* (*Oleum Cubebæ*, U. S. P.), are hydrocarbons, having the formulæ $C_{15}H_{24}$. This *cubebene* is sometimes associated with a camphor, *hydrous cubebene* ($C_{15}H_{24},H_2O$). Oil of cubebs also contains a small quantity of a terpene ($C_{10}H_{16}$). 26. Oil of *Coriander* (*Coriandrum*, U. S. P.; *Oleum Coriandri*, U. S. P.) seems to have the composition of hydrous oil of turpentine ($C_{10}H_{16},H_2O$). 27. The fruits of *Cumin* or *Cummin* (*Cuminum cyminum*), an ingredient of many curry-powders, contain about 3 per cent., and those of *Water Hemlock*, or *Cowbane* (*Cicuta virosa*), about 1¼ per cent., of an essential oil composed of *Cymol* or *Cymene* ($C_{10}H_{14}$) and *Cuminol* ($C_{10}H_{12}O$). The latter is an aldehyd readily uniting with alkaline bisulphites and by oxidation yielding *Cuminic Acid* ($C_{10}H_{12}O_2$). Cymol also occurs in *Garden Thyme* (*Thymus vulgaris*). 27*a*. The fresh flowering herb of *Erigeron canadense*, or Canadian Fleabane, yields an essential oil (*Oleum Erigerontis*, U. S. P.) 28. *Eucalyptus globulus* leaves (*Eucalyptus*, U. S. P.) furnish nearly 1 per cent. of an oil (*Oleum Eucalypti*, U. S. P.) of sp. gr. 0.917, the more volatile and chief portion of which is *eucalyptol* or *cymene*, and a terpene ($C_{10}H_{14} + 2C_{10}H_{16}$), together with an oxidized portion, $C_{10}H_{14}O$ and $C_{10}H_{16}O$. 29. *Elecampane-root*, *Inula Helenium* (*Inula*, U. S. P.), by distillation with water yields solid volatile *helenin* (C_6H_8O), a camphor oil or *inulol* ($C_{10}H_{16}O$), and *inulic anhydride* ($C_{15}H_{22}O_3$). 30. *Oleum Fœniculi*, U. S. P., Oil of *Fennel*-fruit (*Fœniculum*, U. S. P.) differs in odor, but contains the same proximate constituents as oil of anise. 31. Oil of *Geranium*, or *Ginger Grass* oil, from *Andropogon schœnanthus* and various species of *Pelargonium*, contains *geraniol* ($C_{10}H_{18}O$). Oil of *Hedeoma* or American Pennryoyal (*Oleum Hedeomæ*, U. S. P.) has a sp. gr. of about 0.940. 32. *Grains of Paradise* (*Amomum melegueta*), Guinea Grains or Melegueta Pepper, *Semina Cardamomi Majoris*, contain an essential oil ($C_{10}H_{16}$ and $C_{10}H_{16}O$) and a highly pungent resin. 33. Oil of *Juniper* (*Oleum Juniperi*, U. S. P.), the active constituent of Juniper Tops and Berries (*Juniperus*, U. S. P.), contains a hydrocarbon ($C_{10}H_{16}$) which by contact with water yields a white crystalline hydrous compound ($C_{10}H_{16},H_2O$) and a polymeric hydrocarbon ($C_{20}H_{32}$). 34. Oil of *Lavender* (*Oleum Lavandulæ*, U. S. P.), from the flowering tops or whole herb, and *Oleum Lavandulæ Florum*, U. S. P., from the flowers, of *Lavandula vera* (*Lavandula*, U. S. P.), has not been satisfactorily examined. 34*a*. Oil of *Myrcia* (*Oleum Myrciæ*, U. S. P.), oil of bay, or bayberry oil (sp. gr. about 1.040), is obtained from the leaves of *Myrcia acris*. 35. Oil or butter or camphor of *Orris* (*Iris florentina*) is a soft solid lighter than water. Flückiger and Hanbury found it to be chiefly myristic acid associated with a little essential oil. 36. Oil of *Peppermint* (*Oleum Menthæ Piperitæ*, U. S. P.) consists of a hydrocarbon, *menthene* ($C_{10}H_{18}$), different from that of most volatile oils, and hydrous menthene ($C_{10}H_{18},H_2O$), a crystalline stearopten. 37. Oil of *Spearmint* (*Oleum Menthæ Viridis*, U. S. P.), the Common Mint of the kitchen-garden, contains a liquid having the formula $C_{10}H_{20}O$ or $C_{10}H_{18},H_2O$; also, according to Gladstone, *menthol* ($C_{10}H_{14}O$), isomeric with carvol. 38. Oil of *Pennyroyal* (*Mentha pulegium*) contains, according to Kane, $C_{10}H_{16}O$. 38*a*. The leaves and tops of *Melissa officinalis* or *Balm* (*Melissa*, U. S. P.), yield a volatile oil containing a camphor. 39. Oil of *Nutmeg* (*Oleum Myristicæ*, B. P. and U. S. P.), and of the arillus of the nutmeg or mace (*Macis*, U. S. P.), is composed of a hydrocarbon, *myristicene* ($C_{10}H_{16}$), and *myristicol* ($C_{10}H_{16}O$) (Gladstone). 39*a*. Oil of *Origanum*, from *Origanum vulgare*, or *Wild Marjoram* (*Origanum*, U. S. P.), is of a bright yellow and has an odor somewhat like peppermint; it is a mixture of a liquid hydrocarbon and a camphor which is deposited after long standing. 40. Oil or *Otto* or *Attar* of *Cabbage-Rose Petals* (*Rosæ Centifolia*, U. S. P.; *Oleum Rosæ*, U. S. P.) gives the fragrance to rose-water (*Aqua Rosæ*, B. P.). It resembles most other volatile oils in being composed of a hydrocarbon and an oxidized portion, but differs from all in this respect, that the hydrocarbon is solid and is destitute of odor, while the oxygenated constituent is liquid and the source of the perfume. According to Flückiger, the solid hydrocarbon ($C_{16}H_{34}$) yields succinic acid as the chief product of its oxidation by nitric acid, and in other respects affords evidence of belonging to the paraffin series of fats. 41. *Rosmarinus*, U. S. P., Oil of *Rosemary-tops* (*Oleum Rosmarini*, U. S. P.), exists in the plant to the extent of from 1½ to 3 parts per 1000. It chiefly consists of a hydrocarbon ($C_{10}H_{16}$) resembling that from Myrtle, *Myrtus communis*, but also contains oxygenized oil and stearopten ($C_{10}H_{16}O$ and $C_{10}H_{18}O$) in variable proportions. 42. Oil of *Rue* (*Oleum Rutæ*, U. S. P.) contains a small quantity of hydrocarbon ($C_{10}H_{16}$), with some rutic aldehyd ($C_{10}H_{20}O$), but, according to Greville Williams, is chiefly euodic aldehyd ($C_{11}H_{22}O$), some lauric aldehyd ($C_{12}H_{24}O$) also being present. Gorup-Besanez and Grimm have obtained oil of rue ($C_{11}H_{22}O$) artificially as one of the products of the destructive distillation of acetate and caprate of calcium. 43. Oil of *Savine* (*Oleum Sabinæ*, U. S. P.), from the tops of *Juniperus Sabina* or Savine (*Sabina*, U. S. P.), contains several hydrocarbons, but none isomeric with oil of turpentine (Tilden). 43*a*. *Sage* (*Salvia*, U. S. P.) contains about 40 per cent. of *salviol*, $C_{10}H_{16}O$; about 20 per cent. of two $C_{10}H_{16}$ hydrocarbons, boiling at 156° C. and 167° C. respectively; about 10 per cent. of a camphor, $C_{10}H_{16}O$; and about 10 per cent. of cedrene, $C_{15}H_{24}$ (Muir). 44. Oil of *Elder-flowers* (*Sambucus*, U. S. P.) occurs in very small quantity; it has a butyraceous consistence: it contains a hydrocarbon, *sambucene* ($C_{10}H_{16}$), and probably a camphor. 45. Oil of *Sandal-Wood* (*Oleum Santali*, U. S. P.), or oil of *Santal*, has not been thoroughly examined. It occurs to the extent of about 1 per cent. in the fragrant white or yellow sandal-wood of India, *Santalum album*, a small tree of the natural order Santalaceæ, and not to be confounded with the *Pterocarpus santalinus*, a tree of the natural order Leguminosæ, and furnishing the inodorous Red Sandal-Wood or Red Sanders-Wood of the dyer.* 46. Oil of *Sassafras-root*, (*Oleum Sassafras*, U. S. P.), sp. gr. 1.094 (*Sassafras*, U. S. P.), yields *safren* ($C_{10}H_{16}$) and large quantities of a stearopten, *safrol* or *sassafrol* ($C_{10}H_{10}O_2$). 47. Oil of *Mustard* (*Oleum Sinapis Volatile*, U. S. P.) is the sulphocyanate of allyl (p. 453). If adulterated with alcohol its sp. gr. is below 1.015. 48. Oil of *Sweet Flag* (*Acorus calamus*) contains the hydrocarbon $C_{10}H_{16}$. (The rhizome, *Calamus*, U. S. P., also contains *Acorin*, a bitter glucoside.) 48*a*. The tops and leaves of *Thuja occidentalis*, or *Arbor Vitæ* (*Thuja*, U. S. P.), yields two oxygenated oils (also a bitter principle, *pinipicrin*). 49. Oil of *Turpentine* (*Oleum Terebinthinæ*, U. S. P.). Turpentine itself is really an oleo-resin of about the consistence of fresh honey. It flows naturally or by incision from the wood of most coniferous trees, larch (*Larix Europæa*) yielding *Venice turpentine*, *Abies balsameæ* furnishing *Canadian turpentine*, *Balsam of Fir* or *Canada Balsam* (*Terebinthina Canadensis*, U. S. P.), the bark of *Pistachia terebinthus*, the variety termed *Chian Turpen-*

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* *Santalum Rubrum*, U. S. P.

tine (containing about 1 part of essential oil to 7 of resin), and the *Pinus palustris*, *P. australis*, *P. abies*, *P. pinaster*, and *P. tæda* affording the common American turpentine, *Terebinthina*, U. S. P. *Pinus maritima* gives the French or Bordeaux turpentine, and *P. picea*, the old fragrant Strasburg turpentine. By distillation turpentine is separated into *rosin* or *resin* (p. 477), which remains in the still, and *essential oil of turpentine*, often termed simply *turpentine*, *spirit of turpentine*, or "*turps*," which distils over. Mixed with alkali to saturate resinous acids, and redistilled, oil of turpentine furnishes about 80 per cent. of *rectified oil of turpentine*. Under the influence of heat, chemical agents, or both, pure oil of turpentine ($C_{10}H_{16}$) yields many derivatives of considerable chemical interest. The terpene of Bordeaux turpentine (terebenthene) rotates a ray of polarized light more than, and in the opposite direction to, the terpene of American turpentine. 50. Oil of common garden *Thyme* (*Thymus vulgaris*), *Oleum Thymi*, U. S. P., is composed of *cymene* or *cymol* ($C_{10}H_{14}$), *thymene* ($C_{10}H_{16}$), and *thymol* ($C_{10}H_{14}O$) (*Thymol*, U. S. P.). Thymol is also contained in (50*a*.) Oil of *Horsemint* (*Monarda*). Thymol crystallizes out when oil of thyme or of ptychotis, etc. is kept at a low temperature for a day or two. It may also be obtained by shaking the oils with caustic alkali and treating the separated alkaline liquid by an acid. It may be purified by distillation or crystallization from alcohol. It would seem that as an antiseptic thymol is far stronger than carbolic acid. 51. Oil of *turmeric* (*Curcuma longa*) is said by Jackson and Menke to be chiefly an alcohol having the formula $C_{19}H_{27}HO$. They name it *turmerol*. It is a light yellow volatile oil, having the sp. gr. 0.902. It is to this oil that turmeric (and, therefore, curry-powder) owes its flavor and odor. 52. Oil of *Valerian-root* (*Valeriana*, U. S. P.) (*Oleum Valerianæ*, U. S. P.) is a mixture of a hydrocarbon, *valerene* or *borneëne* ($C_{10}H_{16}$), and *valerol* ($C_6H_{10}O$). Valerol slowly oxidizes to valerianic acid, known by its smell. A similar change occurs at once if oil of valerian be allowed to fall, drop by drop, on heated caustic potash: $C_6H_{10}O + 3KHO + H_2O = K_2CO_3 + KC_5H_9O_2 + 3H_2$. By the action of sulphuric acid on the valerianate of potassium thus produced, valerianic acid is obtained. 53. Oil of *Verbena*, *Lemon-Grass* Oil, or *Indian Melissa* Oil, is obtained from *Andropogon citratus* (*Oleum Andropogi Citrati*, P. I.). 54. Oil of *Ginger* (*Zingiber*, U. S. P.) is, according to Thresh, a complex mixture of hydrocarbons and of their oxidation products. Cymene ($C_{10}H_{14}$) is present, a terpene, adehyds, and ethereal salts. (For an analysis of ginger, by Thresh, and for a paper on "Soluble Essence of Ginger," see the *Pharmaceutical Journals* for August 30 and September 6, 1879, and March 4, 1882.) 55. American wormseed (*Chenopodium*, U. S. P.) contains a volatile oil (*Oleum Chenopodii*, U. S. P.).

CAMPHORS.—In addition to the stearoptens or camphors already mentioned as being contained in or formed from volatile oils, there is one that is a common article of trade. It is obtained from the wood of *Cinnamomum camphora*, or Camphor-Laurel, in Japan (termed in Europe "Dutch Camphor," because imported by the Dutch) and in

China (known as "Formosa Camphor") by a rough process of distillation with water, and is purified by resublimation (*Camphora*, U. S. P.). The formula of laurel-camphor is $C_{10}H_{16}O$.; sp. gr. 0.990 to 0.995; melting-point 175° C.; boiling-point 205° C. Bromine heated with camphor gives *monobrom camphor* ($C_{10}H_{15}BrO$) and hydrobromic acid. Monobromated camphor (*Camphora Monobromata*, U. S. P.) is camphor in each molecule of which an atom of hydrogen has been displaced by one of bromine. Recrystallized, it occurs in white prisms. It melts at 65° C. and boils at 274° C. The essential oil from which doubtless camphor is derived by oxidation is easily obtained from the wood, and is occasionally met with in commerce under the name of *liquid camphor* or *camphor oil;* its formula is $C_{20}H_{32}O$; by exposure to air it becomes oxidized and deposits common camphor, $2C_{20}H_{32}O + O_2 = 4C_{10}H_{16}O$. Camphor distilled with phosphoric anhydride yields cymol, $C_{10}H_{14}$. There is another kind of camphor in European markets less common than laurel-camphor, but highly esteemed by the Chinese; it is obtained from the *Dryobalanops aromatica*, and denominated Sumatra or Borneo camphor. It differs slightly from laurel-camphor in containing more hydrogen, its formula being $C_{10}H_{18}O$. It is accompanied in the tree by a volatile oil ($C_{10}H_{16}$) isomeric with oil of turpentine. This oil, *borneëne*, is also occasionally met with in trade under the name of *liquid camphor* or *camphor oil*, but differs from laurel-camphor oil in not depositing crystals on exposure to air.

Camphor is soluble to a slight extent in water (40 grains per gallon, Pooley). The official Camphor-water (*Aqua Camphoræ*, U. S. P.) is such a solution.

Common camphor, and many other of the camphors, oily hydrocarbons, and oxidized hydrocarbons, yield *camphoric acid* ($C_{10}H_{16}O_4$) and *camphoretic acid* ($C_{10}H_{14}O_7$) when attacked by oxidizing agents. Such reactions indicate natural relationships. Camphoric acid is a good antiseptic.

Cantharidin ($C_5H_6O_2$), the active blistering-principle of cantharides (*Cantharis*, U. S. P.) and other vesicating insects (such as *Mylatris cichorii*, or *Telini Fly*, P. I., common in India), has most of the properties of a camphor or stearopten. It slowly crystallizes, from an alcoholic tincture of the beetles, in fusible, volatile, micaceous plates. The following process for the extraction of cantharidin is by Fumouze: Powdered cantharides are macerated with chloroform for twenty-four hours, and this treatment is repeated twice with fresh quantities of solvent, the residue having been well squeezed each time. The collected solutions are then distilled, and the dark-green residue treated with bisulphide of carbon, which dissolves fatty, resinous, and other matters and precipitates the cantharidin. The precipitate is thrown on a filter, washed with bisulphide of carbon, and recrystallized from chloroform. The same process, omitting the final recrystallization, may be used for the quantitative estimation of cantharidin in cantharides. The average quantity found is from 4 to 5, but occasionally from 10 to 12, parts in 1000. Cantharidin is readily soluble in warm glacial acetic acid (Tichborne), and still more readily in acetic ether. Cantharides from which the fat has been removed by petroleum ether yields the cantharidin with great facility.

Massing and Dragendorff consider cantharidin to be an anhydride ($C_5H_6O_2$), and that with the elements of water it forms *cantharidic acid* ($H_2C_5H_6O_3$). A cantharidate of potassium has the composition $KHC_5H_6O_3$. Piccard gives the vapor-density of cantharidin as about 6.5, and its formula $C_{10}H_{12}O_4$.

QUESTIONS AND EXERCISES.

841. How do volatile oils usually differ chemically from fixed oils?

842. What are the general chemical characters of volatile oils?

843. Describe the usual process by which volatile oils are obtained.

844. Mention the differences in composition between the volatile oils of *Anthemis nobilis* and *Matricaria chamomilla.*

845. Give the systematic name of oil of horseradish.

646. State the general composition of the oil of lemon, lime, bergamot, citron, and cedra.

847. Name the constituents of oil of cloves.

848. In what respect does oil (or otto) of roses differ from other volatile oils?

849. To what class of substances do the constituents of oil of rue belong?

850. How does natural turpentine differ from the turpentine of trade?

851. With what object is commercial turpentine rectified?

852. How is camphor oil related to camphor?

853. In what respects do Borneo or Sumatra camphor and camphor oil differ from the corresponding products of Japan and China?

854. What is the nature of cantharidin?

RESINOID SUBSTANCES.

Resins, Oleo-Resins, Gum-Resins, Balsams.

Resins occur in plants generally in association with volatile oils. They closely resemble camphors or stearoptens, but are not volatile, and differ from oils and fats mainly in being solid and brittle. *Oleo-resins* are mixtures of a resin and a volatile oil. *Gum-resins* are mixtures of a resin or oleo-resins and gum. *Balsams* are commonly described as resins or oleo-resins which yield benzoic or cinnamic acid, but oleo-resins containing neither of these acids are often termed balsams; *e. g.*, balsam of copaiva and Canada balsam. A physico-chemical method for the identification of the chief resins, gum-resins, and balsams will be found in the *Pharmaceutical Journal* for Nov. 17, 1877. Resins appear to be somewhat antiseptic. Beer is said never to turn sour in casks lined with Burgundy pitch. The resin of hops has, perhaps, a similar effect in retarding oxidation of alcohol.

RESINS.—1. *Resin*, *rosin*, or *colophony* (*Resina*, U. S. P.) is the type of this class. Its source is the oleo-resin or true turpentine of the conifers, a body which by distillation yields spirit of turpentine and a residuum of rosin. "Brown" and "White" rosin are met with in trade. The former is the residue of American, the latter of Bordeaux, turpentine (from *Pinus abies*, etc. and *Pinus maritima*, respectively). The chief constituents of brown resin are *pinic acid* ($HC_{20}H_{29}O_2$) and *sylvic acid*, identical in composition, but differing in properties (*vide* Isomerism), the former being soluble and the latter insoluble in cold spirit of wine. White resin or "galipot" is chiefly *pimaric acid*, also isomeric with pinic acid. Pinic acid heated yields *colophonic* or *colopholic acid*. Among the products of the destructive distillation of resin Tichborne has found "*colophonic hydrate*" ($C_{10}H_{22}O_3,H_2O$), a white inodorous crystalline substance, and by depriving this of water has obtained white crystalline *colophonine* ($C_{10}H_{22}O_3$). Resin is soluble in oil of turpentine. Contact with sulphuric acid immediately colors it strongly red. 2. *Arnicin* ($C_{20}H_{30}O_4$), the chief acrid if not the only active principle of Arnica (*Arnicæ Radix*, B. P.; *Arnicæ Flores*, U. S. P.), is a resin. 3. *Cannabin*, said to be the active principle of *Indian Hemp* or *Indian Cannabis* (*Cannabis Indica*, U. S. P., the flowering tops of the female plant of *Cannabis sativa*) and *American Cannabis* (*Cannabis Americana*, U. S. P., the *Cannabis sativa* plant grown in the United States), was obtained in 1846 by T. and H. Smith, and is a resin. Personne in 1857 isolated a volatile oil said to possess much medicinal activity, consisting of *cannabene* ($C_{18}H_{20}$) and a solid crystalline "*hydride of cannabene*" ($C_{18}H_{22}$). 4. *Capsicum-fruit* contains resin (p. 479). 5. *Castorin*, a resinous matter, is the name given to the chief constituent of *Castor* (*Castoreum*, B. P.), the dried preputial follicles and included secretion of the beaver (*Castor fiber*). 6. *Copal.* The best copal is the exuded resin of trees of extinct forests, and is found beneath the surface of the ground in the neighborhood of existing trees. It appears to be a mixture of acids, but its character is still obscure. 7. *Dragon's Blood*, a crimson-red resin found as an exudation on the mature fruits of a Rotang or Rattan Palm (*Calamus draco*). It is said to be a definite substance, and to have the formula $C_{20}H_{20}O_4$. 8. *Ergotin* is a very active resinoid constituent of *Ergot* (*Ergota*, U. S. P.), or the "sclerotium (compact mycelium or spawn) of *Claviceps purpurea*, produced within the paleæ of the common rye, *Secale cereale*." Maize or Indian Corn, *Zea mays*, appears to foster a similar parasite, the *Ustilago maydis*, or Corn Smut (*Ustilago*, U. S. P.). According to Wenzell, ergot contains two alkaloids, *ecboline* and *ergotine*, to the former of which, he says, the activity of ergot is due. Blumberg considers these alkaloids to be identical. Tanret states that an unstable alkaloid termed *ergotinine* occurs in ergot, and to the extent of 1 per 1000, and that it is accompanied by a camphor. Dragendorff and Podwissotzky assert that ergot owes most of its activity to *sclerotic* or *sclerotinic acid*, present to the extent of about 4 per cent. No separated principle representing the full activity of ergot has yet been extracted from that drug. The same may be said of a similar therapeutical agent, the root-bark of *Gossypium herbaceum* (*Gossypii Radicis Cortex*, U. S. P.), the activity of which appears to reside in a red resin. 9. *Guaiacum resin* is a mixture of several substances (p. 421). 10. *Jalap resin* (p. 422). 11. *Kousso*, or *Kooso* (*Brayera*, U. S. P.), yields yellow crystals of a resinoid body readily soluble in alkaline liquids, *kosin* or *koussin* ($C_{31}H_{38}O_{10}$). 12. *Mastic* (*Mastiche*, U. S. P.) is a resinous exudation obtained by incision from the stem of the Mastic or Lentisk tree. Nine-tenths of mastic is *mastichic acid* ($C_{20}H_{31}O_2$), a resin soluble in alcohol; the remaining tenth, *masticin* ($C_{20}H_{31}O$), a tenacious elastic resin. 13. *Mezereon* (*Mezereum*, U. S. P.), the dried bark of *Daphne mezereum*, Mezereon, and *Daphne laureola*, Spurge Laurel, owes its acridity to a resin. 14. *Pepper* contains a resin (p. 397). 15. *Burgundy Pitch* (*Pix Burgundica*, U. S. P.) is the melted and strained exudation from the stem of the Spruce Fir, *Abies excelsa*. The term Burgundy is a misnomer, the resin never having been collected at or near Burgundy; Finland, and to a smaller extent Baden, and Austria being the countries whence it is derived. Its constituents closely resemble those of common resin. It is often adulterated and imitated by a mixture of resin with palm oil, water, etc., from which it may be readily distinguished by its duller yellow color, highly aromatic odor, greater solubility in alcohol, and almost complete solubility in twice its weight of glacial acetic acid (Hanbury). 16. *Podophyllum resin.* In preparing the resin of podophyllum, or May-apple (*Resina Podophylli*, U. S. P.), an alcoholic extract of the rhizome and rootlets of *Podophyllum peltatum* (*Podophyllum*, U. S. P.) is poured into cold water acidulated by hydrochloric acid. This resin is the chief active principle of podophyllum-root. According to Guareschi, podophyllin contains a glucoside resembling convolvulin. Podwissotzky has extracted from podophyllin a little coloring-matter, fat, a bitter crystalline acid, a bitter crystalline neutral principle, and an amorphous acid resin. 17. *Pyrethrin* is the name of the acrid resinous active principle of the root of *Anacyclus pyrethrum*, or *Pellitory-root* (*Pyrethrum*, U. S. P.). According to Buckheim, the action of alkalies breaks it up into piperidine and pyrethric acid. (The crystalline poisonous principle obtained by Bellesme from *Pyrethrum carneum*, the powder of which (and of *P. roseum*, and especially *P. cinerariæ folium*, or *Dalmatian Insect-Powder*) is the well-known "insecticide," has not yet been analyzed.) 18. The resins of Rhubarb have already been alluded to in connection with Crysophanic Acid (p. 335). 19. *Rottlerin* is the name given by Anderson to a crystalline resin from Kamala (*Kamala*, U. S. P.), the minute glands that cover the capsules of *Rottlera tinctoria:* to this and, apparently, allied resins, Kamala owes its activity as an anthelmintic.

OLEO-RESINS.—1. *Capsicin*, a term suggestive of a definite chemical substance, is a name somewhat unhappily accorded to an indefinite substance, an oleo-resin, obtained by digesting the alcoholic extract of Capsicum-fruit (*Capsicum*, U. S. P.) in ether and evaporating the clear ethereal fluid to dryness. Besides volatile oil and resin, capsicum-fruits contain much fatty matter, which Thresh states is chiefly free palmitic acid. (See also *Capsicine* and *Capsaicin*, p. 394.) 2. *Copaiva* (*Copaiba*, U. S. P.), sp. gr. 0.940 to 0.993, is a mixture of essential oil ($C_{15}H_{24}$), with 2 or more per cent. of brown soft resin, and 30 to 60 of a yellow dark crystalline resin termed *Copaivic acid* ($C_{20}H_{30}O_2$). Copaiva, containing about equal parts of this acid and of the oil, heated with a fourth of its weight of the official carbonate of magnesium, yields a transparent fluid, owing to the formation of copaivate of magnesium and solution of this soap in the essential oil. With an equal weight of the carbonate enough soap is produced to take up the whole of the essential oil and form a mass capable of being rolled into pills. A much smaller quantity of calcined magnesia, as might be expected, effects the same result; but more time, often several days, is required before complete reaction is effected. The *Massa Copaibæ*, U. S. P., is formed from 6 parts of magnesia and 94 of copaiba. Quicklime has a similar effect. Perhaps carbonate reacts more quickly because of its fine state of division and admixture of hydrate; in which case hydrates of calcium and magnesium may be expected to act better than the calcined preparations, and in much smaller quantity than carbonate of magnesium. Copaiva, unlike, 3, *Wood Oil* or *Gurjun Balsam* (*Dipterocarpi Balsamum*, P. I.), a similar oleo-resin from the *Dipterocarpus turbinatus* (*D. Lævis*, P. I.), does not become gelatinous when heated to 270° F. Copaiva is often slightly fluorescent; Gurjun balsam is highly fluorescent. The stated analogy of Gurjun balsam to copaiva is borne out by its chemical composition, for by distillation it yields about 40 per cent. of an essential oil identical in composition with oil of copaiva, the non-volatile portion being resinous. The adulteration of copaiva with fixed oil is best detected by heating 20 or 30 drops in a capsule until all essential oil has evaporated. Turpentine is betrayed by its odor during this evaporation. The residue, copaiva resin, is brittle if pure, and more or less sticky or soft if fixed oil is present. The limit of brittleness is stated, by Siebold, to be reached when 1 per cent. of oil has been added to the copaiva, that amount preventing the residue being reduced to a fine powder. "The essential oil distilled off from the oleo-resin, when rectified, should not begin to boil below 200° C. (392° F.). On adding 1 drop of copaiba to 19 drops of disulphide of carbon and shaking the mixture with 1 drop of a cold mixture of equal parts of sulphuric and nitric acids, it should not acquire a purplish-red or violet color (absence of gurjun balsam)." —U. S. P. *Resina Copaibæ*, U. S. P., is the residue left after distilling off the volatile oil from copaiba. 4. *Elemi* (*Elemi*, B. P.) is an exudation from a tree growing in the Philippine Islands. It consists of volatile oil ($C_{10}H_{16}$) with 80 or more per cent. of two resins, the one ($C_{20}H_{32}O_2$) soluble in cold alcohol, the other, *amyrin*, $(C_5H_8)_5H_2O$, almost insoluble, associated with *amyric acid*, $(C_5H_8)_7O_4$ (Buri). It also contains small quantities of two crystalline bodies soluble in water, *bryoidin*, $(C_5H_8)_4 3H_2O$, and *breidin* (Flückiger). The *icacin* of Stenhouse and Groves is either identical with amyrin or perhaps has the formula $(C_5H_8)_9H_2O$. All these bodies are probably hydrous terpenes. 5. *Wood-Tar* (*Pix Liquida*, U. S. P.) is a mixture of several resinoid and oily bodies (amongst others Creasote, p. 449) obtained by destructive distillation from the wood of *Pinus sylvestris* and other pines. When heated it yields an almost colorless terebinthinate oil (*Oleum Picis Liquidæ*, U. S. P.), Oil of Tar, sp. gr. 0.970, which soon becomes brown, and a residue of *pitch.* 6. *Turpentines.*—These oleo-resins have been mentioned in connection with oil of turpentine, their volatile, and resin, their fixed, constituent. 7. *Common Frankincense* (*Thus Americanum*, B. P.) is the concrete turpentine of *Pinus tæda.* 8. *Canada Balsam* (*Terebinthina Canadensis*, B. P.), largely gathered in the province of Quebec, is the turpentine or oleo-resin of Balm of Gilead Fir (*Abies balsamea*). 9. *Sumbul-root*, from *Ferula sumbul* (*Sumbul*, U. S. P.), seems to owe its stimulating property to two oleo-resins, one soluble in ether, the other in alcohol. 10. *Oleo-resin of Lupulin* (U. S. P.) is an ethereal extract of the yellow powder (*Lupulinum*, U. S. P.) attached to the small nuts at the base of the scales which form the aggregate fruit of the *Humulus lupulus*, or Hop (*Humulus*, U. S. P.). It contains essential oil of hop (*Valerol*, $C_6H_{10}O$) and oxidized oil or resin, bitter extract containing the hop-bitter, lupulinic acid ($C_{32}H_{50}O_7$), and tannic acid. *Oleoresinæ Aspidii*, *Capsici*, *Cubebæ*, *Piperis*, and *Zingiberis* are official in the United States Pharmacopœia. 11. *Pix Canadensis*, U. S. P., *Canada Pitch* or *Hemlock Pitch*, is the concrete juice of *Abies canadensis.*

GUM-RESINS.—1. *Ammoniacum* (*Ammoniacum*, U. S. P.) is an exudation from the *Dorema ammoniacum.* It contains nearly 20 per cent. of gum, a little volatile oil, and about 70 of resin ($C_{40}H_{50}O_9$—Johnston). 2. *Asafœtida* (*Asafœtida*, U. S. P.) is a gum-resin obtained, by incision, from the living root of *Ferula narthex* and *F. scorodosma.* It contains from 50 to 70 per cent. of a resin which is partly *ferulaic acid* ($C_{10}H_{10}O_4$), 25 to 30 per cent. of gum (about two-thirds arabin, one-third bassorin, p. 113), and 3 to 5 per cent. of volatile oil. At least 60 per cent. of it should be soluble in alcohol. 3. *Euphorbium*, an old drug which is an emetic and purgative resin. It contains an amorphous active resin ($C_{20}H_{32}O_4$), crystalline *euphorbon* ($C_{26}H_{44}O_2$), and mucilage (Flückiger). 4. The ordinary or Siam *Gamboge* (*Cambogia*, U. S. P.) of European trade is obtained from the *Garcinia Hanburii;* the gamboge of India (*Cambogia Indica vel Mysoriensis*, P. I.) from *G. pictoria.* When of best quality it contains about 20 per cent. of a gum and 80 to 75 per cent. of a resin termed *gambogic acid* ($C_{20}H_{23}O_4$). 5. *Galbanum* (*Galbanum*, U. S. P.) contains from 20 to 25 per cent. of gum, about 65 per cent. of resin ($C_{40}H_{54}O_7$), and 3 or 4 per cent. of volatile oil. Moistened with alcohol, and then with hydrochloric acid, galbanum yields a purple color, due, probably, to the production and oxidation of resorcin. Galbanum, heated for some time to 212° F. with hydrochloric acid, the liquid separated and shaken with ether or chloroform, and the latter evaporated, yields somewhat less than 1 per cent. of colorless acicular crystals of *umbelliferone* ($C_9H_6O_3$).* 6. *Myrrh*

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* "Umbelliferone is soluble in water; its solution exhibits, espe-

(*Myrrha*, U. S. P.), an exudation from the stem of *Balsamodendron myrrha*, contains about half its weight of soluble gum (arabinoid), 10 per cent. of insoluble gum (probably bassorin), 2½ of volatile oil, and about 25 per cent. of resin (myrrhic acid). (For a note by R. H. Parker on the spurious gums imported with myrrh, see the *Pharmaceutical Journal* for July 17, 1880.) 7. *Olibanum* (P. I.), *Thus musculum*, or *Arabian Frankincense* (from various species of *Boswellia*), is about one-third gum and nearly two-thirds resin ($C_{40}H_{30}O_6$), with a little hydrocarbon ($C_{10}H_{16}$) and oxidized hydrocarbon volatile oils. It has always been an important ingredient of *incense*—myrrh, storax, benzoin, and such fragrant combustible resinous substances being other constituents. 8. *Scammony* (p. 424).

Gum-resins need only be finely powdered and rubbed in a mortar with water to yield a medical *emulsion*, in which the fine particles of resin are held in suspension by the aqueous solution of gum.

BALSAMS.—1. *Benzoin* (*Benzoinum*, U. S. P.) is obtained from incisions of the bark of *Styrax benzoin*. It contains 12 to 15 per cent. of benzoic acid (p. 332), about 50 per cent. of a resin (a) soluble in ether, 25 to 30 per cent. of a resin (β) soluble in alcohol only, and 3 to 4 per cent. of a resin (γ) soluble in solution of carbonate of sodium. The a resin is considered to be a compound of the β ($C_{40}H_{46}O_9$) and the γ ($C_{30}H_{40}O_5$). The balsams of Peru, Tolu, and Storax differ from benzoin in containing cinnamic (p. 472) in place of benzoic acid; hence they yield, by oxidation, hydride of benzoyl (oil of bitter almonds). 2. *Balsam of Peru* (*Balsamum Peruvianum*, U. S. P.), from the *Myroxylon pereiræ*, is a mixture of oily matter with about one-quarter or one-third of resinous matter and 6 per cent. of cinnamic acid. The oil, by fractional distillation in an atmosphere of carbonic acid gas and under diminished pressure, furnishes *benzylic alcohol* (C_7H_7HO), *benzoate of benzyl* ($C_7H_7C_7H_5O_2$), and *cinnamate of benzyl* ($C_7H_7C_9H_7O_2$) or *cinnaméin* (Kraut). By action of alcoholic solution of potash it yields benzoate and cinnamate of potassium and benzylic alcohol; also *cinnamic alcohol* (C_9H_9HO), otherwise known as *peruvine* or *styrone;* it also often holds in solution *metacinnaméin* or *styracin* ($C_{18}H_{16}O_2$), isomeric with hydride of cinnamyl (C_9H_7OH). The resin of balsam of Peru

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cially on addition of an alkali, a brilliant blue fluorescence which is destroyed by an acid. If a small fragment of galbanum is immersed in water, no fluorescence is observed, but it is immediately produced by a drop of ammonia. The same phenomenon takes place with asafœtida, and to a slight degree with ammoniacum; it is probably due to traces of umbelliferone pre-existing in those drugs. Umbelliferone is also produced from many other aromatic umbelliferous plants, as *Angelica*, *Levisticum*, and *Meum*, when their respective resins are submitted to dry distillation; also from the resin of *Daphne mezereum*. The fluorescence of umbelliferone may be beautifully shown by dipping some bibulous paper into water which has stood for an hour or two on lumps of galbanum, and drying it. A strip of this paper placed in a test-tube of water with a drop of ammonia will give a superb blue solution, instantly losing its color on the addition of a drop of hydrochloric acid." (Flückiger and Hanbury.)

seems to result from the action of moisture on the oil. When mixed with 3 parts of bisulphide of carbon, about 40 per cent. of resin separates, and the liquid portion should be transparent, of a light-brown color and exhibit only a faint fluorescence (abs. of Gurjun balsam).—U. S. P. The constituents of *Vanilla*, U. S. P., the prepared unripe pods of a plant, somewhat resemble those of balsam of Peru. The crystals often found on vanilla are a weak acid substance having the formula $C_{16}H_{16}O_6$ (Carles). 3. *Balsam of Tolu* (*Balsamum Tolutanum*, U. S. P.) is an exudation from incisions in the bark of *Myroxylon toluifera;* in composition it closely resembles balsam of Peru, but is more susceptible of resinification. It contains benzoate and cinnamate of benzyl, cinnamic acid, a little benzoic acid (Busse), and about 1 per cent. of a volatile hydrocarbon, *tolen*, $C_{10}H_{16}$. Old hard balsam of tolu is a convenient source of cinnamic acid, which is extracted by the same process as that by which benzoic acid may be obtained from benzoin—namely, ebullition with alkali, filtration, and precipitation by hydrochloric acid. 4. *Storax* (*Styrax*, U. S. P.) is an oleo-resin obtained from the *Liquidambar orientale.* It contains a volatile oil termed *styrol cinnamene* or *cinnamol* (C_8H_8)—which possibly (Berthelot) is condensed acetylene, $4C_2H_2$—cinnamic acid, styracin or cinnamate of cinnamyl ($C_9H_9C_9H_7O_2$), and a soft and a hard resin. Styrol differs from similar hydrocarbons in being converted into a polymeric solid termed *metastyrol* or *draconyl* on heating to about 400° F. For medicinal use, storax (*Styrax Præparatus*, B. P.) is sometimes purified by solution in alcohol, filtration, and removal of the alcohol by distillation.

Caoutchouc or India-rubber and Gutta-percha.

Caoutchouc is the hardened juice of *Hevea* (*Siphonia*) *braziliensis*, *Castilloa elastica*, *Urceola elastica*, *Ficus elastica*, and other plants (Collins). Heated moderately with sulphur, it takes up 2 or 3 per cent., and forms *vulcanized India-rubber;* at a higher temperature a hard, horny product, termed *ebonite* or *vulcanite*, results. *Gutta-percha* (U. S. P.) is the concrete drop or juice of the *percha* (Malay) tree, the *Isonandra gutta*, and of other sapotaceous plants. It is soluble in chloroform (*Liquor Gutta-percha*, U. S. P.), benzol, and essential oils. White gutta-percha is obtained by precipitating a solution of the ordinary gutta-percha in chloroform by alcohol, washing the precipitate with alcohol, and finally boiling in water and moulding into the desired form while still hot. The official solution of Gutta-percha (*Liquor Gutta-percha*, B. P.) is made by digesting *thin* slices of gutta-percha in 12 parts by weight of chloroform, and then "fining" by shaking with 1 part of carbonate of lead and setting aside till the fluid is clear.

These two elastic substances, in the pure state, are hydrocarbons (xC_5H_4), usually slightly oxidized.

QUESTIONS AND EXERCISES.

855. How do resins occur in nature? Distinguish between resins

and camphors. Mention the points of difference of resins, oleo-resins, gum-resins, and balsams.

856. Name the source and chief constituents of common Resin or Rosin.

857. Enumerate some official articles of which the active constituents are resins.

858. Give the chief distinguishing characters of Burgundy Pitch.

859. What is the average proportion of oil and of resin in the so-called Balsam of Copaiva?

860. Explain the effect of carbonate of magnesium, magnesia, and lime on copaiva.

861. State the nature of Wood-tar.

862. Why do Ammoniacum, Asafœtida, Gamboge, Galbanum, Myrrh, and similar substances give an emulsion by mere trituration with water?

863. In what respect does Benzoin differ from the Balsams of Peru, Tolu, and Storax?

864. What is the chemical nature of India-rubber and Gutta-percha?

865. How is India-rubber *vulcanized* and converted into *ebonite* or *vulcanite?*

COLORING-MATTERS.

The animal, vegetable, and mineral kingdoms abound in substances or pigments which powerfully decompose light, absorbing certain of its constituent colors and reflecting some others. Thus, for example, most leaves contain a body termed chlorophyll, which has the property of absorbing red light and reflecting green; these reflected rays, entering the eye of an observer and striking on the retina (the expanded extremity of the optic nerve), always communicate the same impression to the brain; in popular language, the leaf is said to be green. Art has richly supplemented the number of such natural coloring-matters.

YELLOW.—1. *Chrome yellow* occurs in more than a dozen shades (see *Lead, Chromate of*). 2. *Fustic* or *yellow-wood* is the wood of the *Rhus cotinus*. 3. *Gamboge* (see *Gamboge*). 4. *Ochre* is met with of many tints, under the names of *yellow ochre*, *gold yellow*, *gold earth* or *ochre*, *yellow sienna*, *Chinese yellow*. It is chiefly a mixture of oxyhydrates of iron with alumina and lime. 5. *Orpiment* is a sulphide of arsenicum (As_2S_3). 6. *Persian berries* or *Avignon grains* contain a yellow principle termed *rhamnin* and other crystalline bodies. They are the product of the *Rhamnus infectorius*. 7. *Purree* or *Indian yellow* is said by Stenhouse to owe its color to *purrate* or *euxanthate of magnesium* ($MgC_{42}H_{34}O_{22}$). 8. *Quercitron* is the bark of *Quercus tinctoria* or Black Oak. It contains the yellow glucoside, *quercitrin* ($C_{18}H_{18}O_{10},H_2O$). 9. *Rhubarb* (see *Chrysophanic Acid*, p. 335). 10. *Saffron* (*Crocus*, U. S. P.), the dried stigma and part of the style of *Crocus sativus*, yields *saffranin* or *polychroite*, an orange-red glucoside, which by the action of dilute acids and by other means breaks up, as shown in the following equation, yielding red *crocin* (Weiss):—

$$\underset{\text{Polychroite.}}{C_{48}H_{60}O_{18}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Crocin.}}{2(C_{16}H_{18}O_6)} + \underset{\text{Vol. oil of saffron.}}{C_{10}H_{14}O} + \underset{\text{Sugar.}}{C_6H_{12}O_6}$$

11. *Turmeric*, the rhizome of *Curcuma longa*, owes its yellow color to *curcumin*, a resinous matter, the formula of which is said by Daube to be $C_{10}H_{10}O_3$, and by Iwanof $C_{16}H_{16}O_4$. Jackson and Menke state that curcumin is an acid, and that its formula is $H_2C_{14}H_{12}O_4$. Possibly two yellow pigments are present. 12. *Weld* (*Reseda luteola*) contains a durable yellow matter termed *luteolin* ($C_{20}H_{14}O_3$). 13. *Picric* or *carbazotic acid* (p. 450) is a very powerful yellow dye. 14. Dried and powdered carrots yield to bisulphide of carbon a yellow coloring-matter, "carrotin," which is obtained on evaporating the solvent. It is said to be used in coloring butter.

RED.—1. *Alkanet*, the root of *Alkanna tinctoria*, Tausch, *Anchusa tinctoria*, Desf., yields *anchusin* ($C_{35}H_{40}O_8$), a resinoid matter soluble in oils and fats. 2. *Annato*, *Arnatto*, or *Arnotto*, a paste prepared from the seeds of *Bixa orellana*, contains *bixin*, an orange-red, and *orellin*, a yellow principle. 3. *Brazil-wood* (*Cæsalpinia brasiliensis*) furnishes *brezilin*, the basis of several lakes. *Sapan-wood* and *Cam-wood* probably contain the same substance. 4. *Cinnabar*, Chinese red, Vermilion, or Paris red is mercuric sulphide. 5. *Chrome red* is an oxychromate of lead. 6. *Cochineal* (p. 334). 7. *Madder*, the root of *Rubia tinctorum*, powdered and treated with sulphuric acid and acidulated water to effect the removal of earthy and other inert matters, furnishes a residual powder termed *garancin*. Garancin yields to pure water *alizarin* ($C_{14}H_{18}O_4,3H_2O$), the red, neutral, crystallizable coloring-matter of madder. Alizarin does not exist ready formed in the plant, but is derived by fermentation from rubian, a yellowish resinoid substance. Alizarin is now produced artificially from *anthracene*, one of the solid constituents of coal-tar. 8. *Mulberry-juice* (*Mori Succus*, B. P.) contains a violet-red coloring-matter which has not been chemically examined. 9. *Red lead* (p. 208). 10. *Red oxide of iron*, of shades varying from light to brown-red, is found native. The common names of it are Armenian bole, Berlin red, colcothar, English red, red ochre, burnt ochre, red earth, terra di sienna, mineral purple, stone red, and Indian red. 11. *Red Sanders-wood* or *Red Sandal-wood* (*Santalum rubrum* or *Red Saunders*, U. S. P.), the billets and chips of *Pterocarpus santalinus*, owes its color to *santalin* ($C_{14}H_{12}O_4$), a crystalline resinoid matter. 12. *Red Poppy Petals* (*Rhœdos Petala*, B. P.), from the *Papaver rhœas*, contain a red coloring-principle which has not yet been isolated in a state of purity. The author has sought for morphine in large quantities of the petals, but could not find a trace of that alkaloid. 13. *Red Rose Petals* (*Rosa Gallica*, U. S. P.), and those of the *Cabbage Rose* (*Rosa Centifolia*, U. S. P.), also yield a red substance, which has not been analyzed. 14. *Safflower*, *Dyer's Saffron*, or *Bastard Saffron*, the florets of *Carthamus tinctorius*, contains an unimportant yellow dye and 5 per cent. *carthamin* ($C_{14}H_{16}O_7$), an uncrystallizable red dye, the pigment of the old *pink* *saucers.* Carthamin seems to possess acid characters, and (like silicic acid and other substances) to be soluble in water for a certain time after liberation from its alkaline solution; for fabrics are dyed with safflower by immersion in a bath made of an infusion in dilute alkali neutralized by citric acid immediately before use, the carthamin probably penetrating the cells and vessels of the fibres in a soluble form, there becoming insoluble and imprisoned, and thus giving permanent color to the wool, silk, or other material. Mixed with French chalk, carthamin is used as a cosmetic under the name of *vegetable rouge*—*carmine* being *animal rouge* and *red oxide of iron mineral rouge.* 15. *Lac-dye* is a cheap form of cochineal, and is also yielded by the species of *Coccus*, whose resinous excretion constitutes *lac* (*stick-lac*, *seed-lac*, or *shell-lac*, according to its condition as gathered off the twigs on which it is deposited, or as roughly separated from impurities in seed-like powder or lumps, or as melted and squeezed through bags into shell-like pieces). 16. *Logwood* (*Hæmatoxylon*, U. S. P.) contains a yellow substance, *hæmatoxylin* ($C_{16}H_{14}O_6,H_2O$ or $3H_2O$), which under the influence of air and alkali assumes an intense red color. Under the influence of ammonia and air it yields greenish-violet iridescent scales of *hæmatin* ($C_{16}H_{12}O_6,3H_2O$). 17. *Red enamel* colors, for glass-staining and ceramic operations, are produced either by cuprous silicate or purple of Cassius (p. 243).

Blue.—1. *Cobalt oxide*, precipitated in combination or admixture with alumina or phosphate of calcium, forms *Thénard's blue, cobalt blue*, *Hoffner's blue*, and *cobaltic ultramarine.* 2. *Smalt*, *Saxony blue* or *King's blue*, is rough cobalt glass in fine powder (p. 230). 3. *Copper blue*, *mountain blue*, and *English* or *Hambro' blue* are carbonates or oxycarbonates of copper. 4. *Indigo* (p. 287). 5. *Litmus*, *lichen blue*, *turnsole*, *orchil* or *archil*, and *cudbear* are products of the action of air and alkalies on certain colorless principles, as *orcin* ($C_7H_8O_2$), derived from different species of lichen, *Roccella*, *Variolaria*, and *Lecanora.* 6. *Prussian blue* (p. 338) and *Turnbull's blue* (p. 339), the ferro- and ferridcyanides of iron, are met with under the names of *Erlangen*, *Louisa*, *Saxon*, *Paris*, or *Berlin blue.* 7. *Ultramarine* is made on a large scale by roasting a mixture of fine white clay, carbonate of sodium, sulphur, and charcoal. Its constitution is not well made out. Acids decompose it, sulphuretted hydrogen escaping.

Green.—1. *Cupro-arsenical* green pigments (p. 173). 2. *Chlorophyll*, *Leaf green*, or *Chromule.* (A method of extracting chlorophyll is given under "Extracts," *vide* Index.) It is resinoid, soluble in alcohol and ether, insoluble in water, and, according to Frémy, consists of a blue substance, *phyllocyanin* ($C_{34}H_{68}N_4O_{17}$?), and a yellow, *phylloxanthin;* the yellow tints in fading autumnal leaves, he says, are due to the latter principle, the former being the first to fade. Chlorophyll would probably well repay extended investigation. 3. *Sap-green*, *buckthorn-*, *vegetable-*, or *bladder-green* is obtained by evaporating to dryness a mixture of lime and the juice (*Rhamni Succus*, B. P.) of the berries of the Buckthorn (*Rhamnus* *catharticus*). It is soluble in water, slightly in alcohol, and insoluble in ether and oils. 4. *Green ultramarine* is made by a process similar to that of blue ultramarine. 5. Mixtures of blue and yellow pigments and dyes are common sources of green colors. 6. Glass and earthenware are colored green by oxide of chromium and black oxide of copper.

BROWN.—1. *Umber*, *Sienna*, or *Chestnut brown* is found native. By heat it is darkened in tint, and is then known as *burnt umber*. It is a mixture of oxide of iron, silica, and alumina. 2. *Sepia* is a dried fluid from the ink-bag of cuttle-fishes (*Sepiadæ*); by its ejection into adjacent water the animal obtains opportunity of escape from enemies. 3. *Catechu* (p. 355) furnishes a brown coloring-matter.

BLACK.—1. *Black-lead* (p. 30), *boneblack* (p. 110) or *ivory-black*, and *lampblack*, the latter a deposited soot from incomplete combustion of resin and tar, are varieties of carbon. 2. *Burnt sugar* or *caramel* (p. 415). 3. *Indian ink* is usually a dried mixture of fine lampblack and size or thin glue. 4. *Black ink* is essentially tannates and gallates of iron suspended in water containing a little gum in solution. 5. *Printer's ink* is well-boiled linseed or other oil mixed with good lampblack, vermilion, or other pigment. 6. *Black dyes* are of the same nature as ink. 7. The *pigmentum nigrum* of black feathers, such as those of the common rook, of dark hair, and probably also of the skin of the negro, seems to be due to the black substance which remains undissolved when black feathers are digested for some time in dilute sulphuric acid. It is said to have the formula $C_{18}H_{16}N_2O_8$ (Hodgkinson and Sorby).

WHITE PIGMENTS.—1. *Chalk* or *Whiting* (p. 108). 2. *French chalk*, *steatite*, or *soapstone*, a silicate of magnesium. 3. *Heavy white* (p. 101). 4. *Pearl-white* (p. 248). 5. *Plaster of Paris* (p. 113). 6. *Starch* (p. 401). 7. *White-lead* (p. 206). 8. *Zinc-white* (p. 131). 9. Oxides of tin and zinc and phosphate of calcium are employed for giving a white opacity to glass.

ANILINE COLORS.—*Coal-tar Colors.*—Within the last ten years nearly every shade of color seen in the animal and vegetable kingdoms has been successfully imitated by certain dyes and pigments primarily derived from a mineral, coal. Coal distilled for gas furnishes tar or gas-tar. Coal-tar contains some aniline, but especially it contains a liquid convertible into aniline—namely, benzol (C_6H_5H), first discovered by Faraday in compressed oil-gas. From aniline, by oxidation, Runge obtained the violet color-reaction, the body producing which Perkin afterward studied and isolated, and manufactured under the name of *mauve*. *Aniline red* (*fuchsine*, *magenta*, or *rosaniline*), *aniline yellow*, *aniline green*, *aniline blue*, and, in short, aniline dyes, lakes, and pigments of every hue of the rainbow, are now common articles of trade. Their application has revolutionized the arts of the dyer and color-printer. The dyeing power of aniline colors may be used in testing for their presence in colored wines (claret, port, etc.).

QUESTIONS AND EXERCISES.

866. Explain the production of color by various natural and artificial pigments.

867. Mention the chief yellow coloring-matters, and describe their chemical nature.

868. What is annatto?

869. Name the colorific constituent of madder. Can it be made artificially?

870. State the source of Litmus.

871. Distinguish between Prussian blue and Turnbull's blue, and state how they are manufactured.

872. How is blue ultramarine obtained? How is it affected by acids?

873. Describe the chemical nature of the coloring-principle of green leaves.

874. By what agents is glass colored green?

875. Whence is sepia obtained?

876. Describe the chemistry of black ink.

877. Write a few sentences on *aniline colors.*

QUALITATIVE ANALYSIS OF SUBSTANCES HAVING UNKNOWN PROPERTIES.

Substances are presented to the analyst in one of the three forms in which all matter exists—namely, solid, liquid, or gaseous—and they may contain animal or vegetable as well as mineral matter.

The method of analysis in the case of *solid mineral bodies* has been described on pp. 367 to 374.

Solid animal or vegetable substances (or mixtures of these with mineral bodies) may be indefinite and beyond the grasp of chemistry, or definite and quite within the range of proximate qualitative organic analysis. The presence of such substances is indicated in the preliminary examination of a solid (pp. 367 to 369) by charring and other characters. If no charring occurs and no volatile liquid is expelled by heat, the absence of such matter is indicated. But if organic matter is present, an endeavor is made to ascertain its precise character. The analyst's knowledge of the history of the substance or the circumstances under which it comes into his hands will probably afford a clue to its nature and enable him to search directly for its proximate constituents. If no such information is at hand, the action of solvents may be employed, as likely to afford indication of the general, if not of the precise, nature of the substance. Water, alcohol, ether, chloroform, bisulphide of carbon, each both hot and cold, may in turn be agitated with the substance, the mixture filtered, a portion of the filtrate evaporated, at first partially, setting the product aside, and afterward to dryness, and any deposit or residue examined with and without the aid of a microscope. Other portions of the filtrate may be treated with acids, alkalies, and solutions of such metallic salts as are commonly used as group-tests for acidulous radicals (p. 364). The action of alkalies, as well as acids, weak and strong, hot and cold, may also be tried on the solid substance itself, and colors, odors, and, in short, any effect whatever, duly noted. A portion of the substance should also be burnt in an open porcelain crucible until no carbon remains, and the ash, if any, examined; its amount and nature may afford information leading to the identification of the substance.

The foregoing experiments having been carefully performed and all results entered in the note-book, a little reflection will possibly lead to the recognition, or may suggest further direct experiments or confirmatory tests, or will, at least, have pointed to the absence of 90 or 95 per cent., of all possible substances, and thus have restricted the area of inquiry to narrow limits. The success attainable in qualitative proximate organic analysis by the medical or pharmaceutical student will of course largely depend on the thoroughness with which the operator has prosecuted his study of practical chemistry generally, but it also will be considerably affected by the extent to which he has cultivated the art of observation, and the opportunities he has had of acquiring a knowledge of the appearances, uses, and common properties of definite chemical substances and of articles of food, drink, and medicine. The most successful of several good analysts will be the one who has most common sense and most experience.

The pharmaceutical student, who has probably already had some years of experience in pharmacy, occupies an unusually favorable position for prosecuting the proximate analysis of organic and inorganic substances, or, at all events, of that large proportion of such bodies met with in the domain of hygiene and pharmacy. Many substances he will identify at sight or by aid of a lens, or after applying some simple physical or chemical test. Nor should he find much difficulty, after reaching the present point of practical study, in deciding whether the solid substance under examination belongs to the class of organic acids, organic salts of metallic radicals, alkaloids, salts of alkaloids, amylaceous matter, gums, saccharine substances, glucosides, albumenoid matters, fats, soaps, resins, coloring-matters, etc. For instance, the pharmaceutical student will find less difficulty than the general student in successfully analyzing a substance occurring in "scales," because he has experience of the appearances of compounds commonly produced in that form, and because, even if the appearance is new to him, he knows what kind of substances most readily lend themselves to production in that form. While the general student is testing generally and proceeding cautiously, or searching for general information in books of reference, the pharmaceutical or medical student has incinerated some of the material, noticed whether or not the ash is red (iron) and strongly alkaline (potassium), treated more of the material with an alkali (for ammonium), added excess of ammonia, and examined the precipitate (for cinchonine or quinine), or shaken up the alkaline liquid successively with ether and chloroform, and tested the residue of these decanted and evaporated solvents (quinine, beberine, strychnine), and examined the aqueous solution of the material or one of the filtered alkaline liquids in the usual way for acidulous radicals (citric, tartaric, sulphuric, hypophosphorous); or he has modified his methods to include search for some "scale preparation" which his special knowledge tells him has been newly introduced to, or is rare in, pharmacy.

In the case of liquids the solvents as well as the dissolved matters claim attention. A few drops are evaporated to dryness on platinum foil to ascertain if solid matter of any kind is present; the liquid is tested by red and blue litmus-paper to ascertain if free alkalies, free acids, or neither, are present; a few drops are heated in a test-tube and the odor of any vapor noticed, a piece of glass tubing bent to a right angle being, if necessary, adapted to the test-tube by a cork, and some of the distilled liquid collected and examined; finally, the usual group-reagents for the several basylous and acidulous radicals are consecutively applied.

Proceeding in this way, the student, who has already had some experience in pharmacy, will not be likely to overlook such solvents as water, acids, alkalies, alcohol, glycerin, ether, chloroform, benzol, fixed oils, and essential oils, or to miss the substances which these menstrua may hold in solution. He will probably also recognize such liquids as carbolic acid, formic acid, lactic acid, methylic alcohol, aldehyd, aniline, nitrobenzol. He must not, however, suppose that he will always be able to qualitatively analyze, say, a bottle of medicine, for the various infusions, decoctions, tinctures, wines, syrups, liniments, confections, extracts, pill-masses, and powders contain vegetable matters, most of which at present are quite beyond the reach of the analyst. Neither the highest skill in analysis, nor the largest amount of experience concerning the odor, appearance, taste, and uses of drugs, is sufficient for the detection of all these vegetable matters. Skill and experience combined, however, will do much, and in most cases even so difficult a task as the one just mentioned be accomplished with reasonable success. Obviously, qualitative analysis alone will not enable the experimenter to produce a mixture of substances similar to that analyzed; to this end recourse must be had to quantitative analysis, a subject reserved for subsequent consideration.

Natural fluids, as "Milk" and "Urine" (*vide* Index), admit of special analytical treatment.

Gas-analysis, or *Eudiometry* (from *εὔδῖα*, *eudia*, calm air, and *μέτρον*, *metron*, a measure, in allusion to the *eudiometer*, an instrument used in measuring the proportion and, as the early chemists thought, the salubrity of the gases of the air), is a branch of experimental investigation, chiefly of a quantitative character, concerning which information must be sought in other treatises. The analysis of atmospheric air from various localities, coal-gas and gases obtained in chemical researches, involves operations which are scarcely within the sphere of Chemistry applied to Medicine. Beyond the recognition, therefore, of oxygen, hydrogen, nitrogen, carbonic, sulphurous, and hydrosulphuric acid gases, the experimental considerations of the chemistry of gaseous bodies may be omitted. Their study, however, should not be neglected, as existing conceptions of the constitution of chemical substances are largely dependent on the observed relations of the volumes of gaseous compounds to their elements. (See previous paragraphs, pp. 36 to 43, 54 to 58, and 155.) The best single work on this latter part of the subject is a small book by Hofmann, *Introduction to Modern Chemistry*.

Spectral Analysis.—It may be as well to state here that the preliminary and final examinations of minute quantities of solid matter may, in certain cases, profitably include their exposure to a temperature at which they emit light, the flame being physically analyzed by a spectroscope. A spectroscope consists essentially of a prism to decompose a ray of light into its constituent colors, with tubes and lenses to collect and transmit the ray or rays to the eye of an observer. The material to be examined is placed on the end of a platinum wire, which is then brought within the edge of a spirit-lamp or other smokeless flame; volatilization, attended usually in the case of a compound by decomposition, at once occurs, and the whole flame is tinged with a characteristic hue. A flat ribbon of rays is next cut off by bringing near to the flame a brass tube the cap of which is pierced by a narrow slit. At the other end of the tube, at focal distance for parallel rays, is a lens through which the ribbon of light passes to a prism; the prism decomposes the ribbon, spreading out its constituent colors like a partially-opened fan, and the colored beam or *spectrum* thus produced is then examined by help of a telescope attached by a movable joint to the stand which carries the prism and object-tube. Sodium compounds under these circumstances give yellow light only, indicated by a double band of light in a position corresponding to a portion of the yellow part of an ordinary solar spectrum. The potassium spectrum is mainly composed of a red and violet band; lithium, a crimson, and at very high temperatures a blue band. Most of the other elements give equally characteristic spectra.

By aid of a combined microscope and spectroscope (microspectroscope) the color of colored fluids can be analyzed.

CHEMICAL TOXICOLOGY.

In cases of criminal and accidental poisoning the substances presented to the chemical analyst for examination are usually articles of food, medicines, vomited matters, or the liver, kidney, intestines, stomach and contents, removed in course of post-mortem examination. In these cases some special operations are necessary before the poison can be isolated in a state of sufficient purity for the application of the usual tests; for in most instances the large quantity of animal and vegetable—or, in one word, organic—matter present prevents or masks the characteristic reactions on which the tests are founded. These operations will now be described;* they form the chemical part of the subject of Toxicology (*τοξικὸν*, *toxicon*, poison, and *λόγος*, *logos*, discourse).

Substances occurring in the form of an apparently definite salt or unmixed with organic matter need no special treatment; they are analyzed by the ordinary methods already given, attention being restricted to poisonous compounds only.

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* Materials for these experiments are readily obtained for educational purposes by dissolving the poison in infusions of tea or coffee, in porter, or in water to which some mucilage of starch, or linseed-meal, pieces of bread, potato, and fat have been added.

EXAMINATION OF AN ORGANIC MIXTURE SUSPECTED TO CONTAIN MERCURY, ARSENICUM, ANTIMONY, LEAD, COPPER, OR ZINC; SULPHURIC ACID, NITRIC ACID, HYDROCHLORIC ACID, OXALIC ACID, OR HYDROCYANIC ACID; CAUSTIC ALKALIES; PHOSPHORUS; STRYCHNINE, MORPHINE, OR OTHER POISONOUS ALKALOIDS.

Preliminary Examination.

Odor, Appearance, Taste.—Smell the mixture, with the view of ascertaining the presence or absence of any notable quantity of free hydrocyanic acid. Look carefully for any small solid particles, such as arsenic, corrosive sublimate, or verdigris, and for any appearance which may be regarded as abnormal, any character unusual to the coffee, tea, beer, medicine, vomit, coats of stomach, kidney, liver, or other organ, tissue, or solid matter under examination.

Poisonous Quantity of Acid.—Add to a small portion some solution of carbonate of sodium, with the view of ascertaining by strong effervescence the presence of any large, poisonous quantity of sulphuric, nitric, or hydrochloric acid (p. 495).

Poisonous Quantity of Alkali.—If so excessively alkaline as to require the addition of a very large quantity of acid before neutralization is effected, a noxious quantity of a corrosive or caustic alkali is present. Whether soda or potash, is ascertained by the usual tests.

Special instructions may induce the operator to suspect the presence of one particular poison. Direct examination for the latter may then be made, either at once if the substance has an aqueous character, or when filtration or treatment with warm hydrochloric or acetic acid has afforded a more or less colorless liquid.

Fluids.—A vomit or the contents of a stomach, if set aside in a long narrow vessel (test-glass or ale-glass), or, better, exposed on a filter during a night, will often yield a more or less clear limpid portion at the bottom or top of the solid matter. This fluid (separated by a pipette or otherwise) will sometimes respond to tests without further preparation, and always requires less preparatory treatment than a semi-solid mixture. If none passes through a filter, a portion often collects in the upper part.

General Procedure.—If the preliminary examination does not indicate the method to be pursued, proceed as follows, treating a portion (not more than one-fourth) of the mixture for the poisonous metals, another for the acids, and a third for alkaloids, reserving the remainder for any special experiments which may suggest themselves in the course of analysis:—

Examination for Mercury, Arsenicum, Antimony, Lead, Copper, Zinc.

If a liquid, acidulate with hydrochloric acid and boil for a short time. If solid or semi-solid, cut up the matter into small pieces, add enough water to form a liquid mixture, stir in 10 or 20 per cent. of ordinary liquid hydrochloric acid, and boil until, from partial aggregation and solution of the solid matter, filtration can be easily effected.

Heat a portion of the clear liquid with a thin piece of bright pure copper or copper gauze about an inch long and a quarter of an inch broad for about ten or twenty minutes; metallic *mercury*, *arsenicum*, or *antimony* will be deposited on the copper, darkening it considerably in color. Pour off the liquid from the copper, carefully rinse the latter with a little cold water, dry the piece of metal by holding it over or near a flame (using fingers, not tongs, or it may become sufficiently hot for loss of mercury or arsenicum to occur by volatilization), introduce it into a narrow test-tube or piece of glass tubing closed at one end, and heat the bottom of the tube in a flame, holding it horizontally, that the upper part of the tube may be kept cool, and partially closing the mouth with the finger to prevent escape of vapor. Under these circumstances any *mercury* will volatilize from the copper and condense on the cool part of the tube in a ring or patch of white sublimate, readily aggregating into visible globules on being pressed by the side of a thin glass rod inserted into the tube; *arsenicum* will volatilize from the copper, and, absorbing oxygen from the air in the tube, condense on the cool part of the glass in a ring or patch of white sublimate of arsenic (gray, or even darker if much arsenicum as well as arsenic be present), not running into globules when rubbed, but occurring in small crystals, the characteristic octahedral form of which is readily seen by aid of a good hand-lens or the lower part of a microscope; *antimony* volatilizes from the copper if strongly heated, and, absorbing oxygen, immediately condenses as a slight white deposit close to the metal.

Confirmatory Tests.—1. Nothing short of the production of globules should be accepted as evidence of the presence of mercury. It will usually have existed as corrosive sublimate.

2. To confirm indications of the presence of arsenicum, a portion of the acid liquid may be subjected to the hydrogen tests (pp. 169,

170), or the tube containing the white crystalline arsenic may be broken, and the part on which the sublimate occurs boiled for some time in water, and the hydrosulphuric-acid, ammonio-nitrate-of-silver, and ammonio-sulphate-of-copper tests (pp. 172, 174) applied to the aqueous solution.

3. For antimony a portion of the acid liquid must always be introduced into the hydrogen apparatus with the usual precautions. (*Vide* p. 184.)

Note.—Before finally concluding that arsenicum is absent from a fluid the latter should be warmed with a little sulphurous acid, and ordinary tests then again applied, for arsenic acid and other arseniates are not readily affected by the usual reagents for arsenicum.

For *lead* or *copper*, pass hydrosulphuric acid gas through the clear acid liquid for some time, warming the liquid if no precipitate is produced, or diluting and partially neutralizing the acid by ammonia if much acid has been added. Collect on a filter any black precipitate that may have formed; wash, dissolve in a few drops of aqua regia, dilute, and apply the tests, such as ammonia for copper, sulphuric acid for lead, and any other of the ordinary reagents (pp. 189, 210).

Copper may often be at once detected in a small quantity of acidulated liquid by immersing the point of a penknife or a piece of bright iron wire—a deposit of copper, in its characteristic color, quickly or slowly appearing, according to the amount present (p. 189).

Zinc.—To the acid liquid through which sulphuretted hydrogen has been passed, add excess of ammonia (or to the original acid fluid add excess of ammonia and then sulphydrate of ammonium); a precipitate falls which may contain alumina, phosphates, and zinc; it is usually blackish from the presence of sulphide of iron. Collect the precipitate on a filter, wash, dissolve in a little hydrochloric acid, add a few drops of nitric acid, boil, pour in excess of ammonia, filter, and test the filtrate with sulphydrate of ammonium: a white precipitate indicates zinc.

Examination for Mineral Acids, Oxalic Acid, or Hydrocyanic Acid.

To detect *Hydrochloric*, *Nitric*, or *Sulphuric Acid* in any liquid containing organic matter, dilute with water and apply to small portions the usual tests for each acid, disregarding indications of small quantities. (*Vide* pp. 264, 286, 307.)

Excessive sourness, copious evolution of carbonic acid gas on the addition of carbonate of sodium, and abundant evidence of acid on applying the various tests to small portions of the fluid presented for analysis, collectively form sufficient evidence of the occurrence of a poisonous amount of either of the three common mineral acids. Small quantities of the hydrochloric, nitric, and sulphuric radicals occurring as metallic salts or acids are common normal constituents of food, hence the direction to disregard insignificant indications. If the fluid under examination be a vomit or the contents of a stomach, and an antidote has been administered, free acid will not be found, but, instead, a large amount of corresponding salt.

For *oxalic acid*, filter or strain a portion of the liquid, if not already clear, and add solution of acetate of lead so long as a precipitate occurs; collect the precipitate, which is partly oxalate of lead, on a filter, wash, transfer it to a test-tube or test-glass, add a little water, and pass hydrosulphuric gas through the mixture for a short time; the lead is thus converted into the insoluble form of sulphide, while oxalic acid is set free in the solution. Filter, boil to get rid of hydrosulphuric gas, and apply the usual tests for oxalic acid (see p. 314) to the clear filtrate.

The contents of a stomach containing oxalic acid are often of a dark-brown color with a tinge of green (altered blood and mucus), and the viscid mixture generally, though slowly, affords some clear, limpid, almost colorless liquid by filtration or standing.

For *hydrocyanic acid* the three chief tests may be applied at once to the liquid or semi-liquid organic mixture, whether it has an odor of hydrocyanic acid or not. First: Half fill a small porcelain crucible with the material, add eight or ten drops of strong sulphuric acid, stir gently with a glass rod, and invert over the mouth of the crucible a watch-glass moistened with a small drop of solution of nitrate of silver; a white film on the silver solution is probably cyanide of silver, formed by the action of the gaseous hydrocyanic acid on the nitrate of silver. Second: Prepare a small quantity of the organic mixture as before, slightly moistening the centre of the watch-glass with solution of potash; here, again, the heat generated by the action of the strong acid is sufficient to volatilize some of the hydrocyanic acid, which, reacting on the potash, forms cyanide of potassium. On removing the watch-glass and stirring into it successively solution of a ferrous salt, a ferric salt, and hydrochloric acid, flocks of Prussian blue are produced if hydrocyanic acid is present. Third: Proceed as before, moistening the watch-glass with sulphydrate of ammonium; after exposure to the hydrocyanic gas for five or ten minutes add a drop of solution of ammonia, evaporate to dryness at a low temperature, and add a drop of hydrochloric acid and of solution of perchloride of iron; a blood-red color, due to sulphocyanate of iron, is produced if cyanogen is present.

If the above reactions are not well marked, the organic mixture may be carefully and slowly distilled in a small retort, the neck of which passes into a bottle and dips beneath the surface of a little water at the bottom of the bottle, and the reagents then applied to separate portions of the distillate.

The examination of organic mixtures for hydrocyanic acid must be made without delay, as the poison soon begins to decompose, and in a day or two is usually destroyed.

Examination for Phosphorus.

A paste containing phosphorus is commonly employed for destroying vermin. In cases of poisoning the phosphorus is commonly in sufficient quantity to be recognized by its characteristic unpleasant smell. A stomach in which it occurs not unfrequently exhibits slight luminosity if opened in a dark room. When the phosphorus is too small in quantity or too much diffused to afford this appearance, a portion of the material is placed in a flask, water acidulated by sulphuric acid added, a long wide glass tube fitted to the neck of the flask by a cork, and the mixture gently boiled. If phosphorus is present (even 1 part in 2,000,000, according to De Vrij) the top of the column of steam as it condenses in the tube will appear distinctly phosphorescent when viewed in a dark room. From its liability to oxidation, phosphorus cannot be detected after much exposure of an organic mixture to air.

Examination for Strychnine and Morphine.

Strychnine.—If solid or semi-solid, digest the matter with water and about 10 per cent. of hydrochloric acid till fluid; filter, evaporate to dryness over a water-bath. If the organic mixture is already liquid, it is simply acidulated with hydrochloric acid and evaporated to dryness. The acid residue is next treated with spirit of wine as long as anything is dissolved, the filtered tincture evaporated to dryness over the water-bath, and the residue digested in water and filtered. This slightly acid aqueous solution must now be rendered alkaline by ammonia, and well shaken in a bottle or long tube with about half an ounce of chloroform, and set by till the chloroform has subsided. The chloroform (which contains the strychnine) is then removed by a pipette, the presence of any aqueous liquid being carefully avoided, and evaporated to dryness in a small basin over a water-bath, the residue moistened with concentrated sulphuric acid, and the basin kept over the water-bath for several hours. (It is highly important that the sulphuric acid used in this operation should be free from nitrous compounds. Test the acid, therefore, by adding powdered sulphate of iron, which becomes pink if nitrous bodies are present. If these are found, the acid should be purified by strongly heating with sulphate of ammonium, 70 or 80 grains to a pint.) The charred material is exhausted with water, filtered, excess of ammonia added, the filtrate shaken with about a quarter of an ounce of chloroform, the mixture set aside for the chloroform to separate, and the chloroform again removed. If, on evaporating a small portion of this chloroform solution to dryness, adding a drop of sulphuric acid to the residue, and warming, any darkening in color or charring takes place, the strychnine is not sufficiently pure for chemical detection; in that case the rest of the chloroform must be removed by evaporation and the residue redigested in warm sulphuric acid for two or three hours. Dilution, neutralization of acid by ammonia, and agitation with chloroform are again practised, and the residue of a small portion of the chloroform solution once more tested with sulphuric acid. If charring still occurs, the treatment must be repeated a third time. Finally, a part of the chloroform solution is taken up by a pipette, and, drop after drop, evaporated on one spot of a porcelain crucible-lid until a fairly distinct dry residue is obtained. A drop of sulphuric acid is placed on the spot, another drop placed near, a minute fragment of red chromate of potassium placed in the second drop, and, when the acid has become tinged with the chromate, one drop drawn across the other; the characteristic evanescent purple color is then seen if strychnine is present. Other tests (*vide* p. 389) may be applied to similar spots.

This is Girdwood and Rogers's method for the detection of strychnine when mixed with organic matter. It is tedious, but trustworthy, and, though apparently complicated, very simple in principle; thus, strychnine is soluble in acidulated water or alcohol or in chloroform, readily removed from an alkaline liquid by agitation with chloroform, and not charred or otherwise attacked when heated to 212° F. with sulphuric acid: much of the organic matter of the food is insoluble in water; of that soluble in water, much is insoluble in alcohol; and of that soluble in both menstrua, all is charred and destroyed by warm sulphuric acid in a shorter or longer time.

Morphine, and the Meconic Acid with which it is Associated in Opium.—To the liquid or the semi-fluid mixture warmed for some time in a small quantity of acetic acid, filtered and concentrated if necessary, add solution of acetate of lead until no further precipitate is produced. Filter and examine the *precipitate* for meconic acid, reserving the *filtrate* for the detection of morphine.

The Precipitate.—Wash the *precipitate* (meconate of lead, etc.) with water, place it in a test-tube or test-glass with a small quantity of water, pass hydrosulphuric acid gas through the mixture for a short time, filter, slightly warm in a small basin, well stirring to promote removal of excess of the gas, and add a drop of neutral solution of perchloride of iron; a red color, due to the formation of meconate of iron, is produced if meconic acid is present. This color is not destroyed on boiling the liquid, as is the case with ferric acetate, nor is it bleached by solution of corrosive sublimate, thus distinguishing it from the ferric sulphocyanate. It is discharged by hydrochloric acid.

The Filtrate.—The solution from which meconic acid has been removed by acetate of lead is evaporated to a small bulk over a water-bath, excess of carbonate of potassium added, and evaporation continued to dryness. The residue is then treated with alcohol, which dissolves the morphine. The alcoholic solution evaporated similarly may leave the morphine sufficiently pure for the application of the usual tests (*vide* p. 381) to small portions of the residue. If no reaction is obtained, add a drop of sulphuric acid and a little water to the residue and shake with ether, in which the salt of morphine is insoluble. The treatment with ether may be repeated until nothing more is removed, the acid aqueous liquid saturated with carbonate of potassium, the mixture evaporated to dryness, the residue digested in alcohol, filtered, and portions of the alcoholic liquid evaporated to obtain spots of morphine for the application of the ordinary tests.

If much organic matter is believed to remain in the filtrate after the acetate-of-lead treatment, or if a considerable excess of acetate of lead has been employed, the filtered liquid should be subjected to a current of sulphuretted hydrogen until no more sulphide of lead is precipitated, the mixture filtered, and the filtrate, with the washings from the sulphide of lead, evaporated to a small bulk, excess of carbonate of potassium added, the whole well mixed and agitated with twice or thrice its bulk of a mixture of ether and acetic ether (ether alone might not dissolve the morphine). On standing, the ethereal liquid rises to the surface; it is carefully removed, evaporated to dryness, and the residue tested or further purified in the manner described in the preceding paragraph.

The examination for morphine must be conducted with great care, and with as large a quantity of material as can be spared, for its isolation from other organic matter is an operation of considerable difficulty, especially when only a minute proportion of alkaloid is present. Fortunately, the detection of meconic acid does not include similar difficulties, and, as its reactions are quite characteristic, its presence is held to be strong evidence of the existence of opium in an organic mixture.

Examination for other Poisonous Alkaloids.

Stas's Process.—Minutely subdivide any solid matter; to this and the liquid portion of the vomit, etc. add about twice their weight of the strongest spirit of wine containing sufficient tartaric acid to fairly acidify the mixture. Digest the whole in a flask at a temperature of 150° or 160° F.; set aside to cool; filter. The solution, which will contain the whole of the alkaloid, should then be evaporated to dryness *in vacuo*, or at all events at a temperature not exceeding 100° F., lest volatile alkaloids should be dissipated. The residue is next exhausted with cold anhydrous alcohol, filtered, and the filtrate evaporated to dryness with the precautions already stated. The extract is dissolved in a very small quantity of water, treated with excess of powdered bicarbonate of sodium or potassium, and well shaken with five or six times its volume of pure ether (with perhaps a little acetic ether). This ethereal liquid contains the alkaloid. Small portions should be evaporated in watch-glasses and tasted, or tested physically and chemically, according as the knowledge of collateral circumstances by the operator, or his experience or such reactions as are recorded on pp. 391–399, may suggest.

If a volatile alkaloid (coniine, nicotine, hyoscyamine, lobeline) is indicated, the ethereal solution, which may still contain animal matter, is removed, agitated with aqueous solution of potash, decanted, and shaken with pure diluted sulphuric acid. On standing, the aqueous portion, containing the alkaloid as acid sulphate, subsides; the upper ethereal portion containing the animal matter is rejected; the acid aqueous liquid is made alkaline with caustic potash or soda; ether added; well shaken; the ethereal liquid decanted, evaporated to dryness *in vacuo* or at a low temperature, and (to get rid of all traces of ammonia) again moistened with ether and dried. The residue is now tested for the suspected alkaloid by taste, smell, and the application of appropriate reagents (pp. 391–399).

If a non-volatile alkaloid (aconitine, atropine, brucine, colchicine, emetine, physostigmine, solanine, veratrine, as well as morphine, codeine, and strychnine) is indicated, further purification is effected by decanting ethereal liquid from the lower aqueous solution of bicarbonate of sodium, removing the ether by evaporation, digesting the residue in alcohol, filtering, evaporating the alcohol, treating the residue with dilute sulphuric acid, setting aside for a few hours, filtering, concentrating, adding powdered carbonate of potassium, and finally anhydrous alcohol. The alcoholic liquid, on evaporation, yields the alkaloid in a fit state for testing in the manner already stated.

Sonnenschein's Process.—Digest with diluted hydrochloric acid, evaporate to the consistence of syrup, dilute, set aside for some hours, filter. Add solution of phosphomolybdic acid so long as any precipitate falls or cloudiness occurs; collect the precipitate on a small filter; wash it with water containing phosphomolybdic and nitric acid, and, while still moist, place it in a flask. Decompose this compound of phosphomolybdic acid and alkaloid by adding caustic baryta until the stirred mixture is distinctly alkaline. Distil off volatile alkaloids, condensing and collecting by help of a long tube so bent that the apparatus shall act as a retort, the end of the tube being attached to a bulb or series of bulbs containing dilute hydrochloric acid. The acid liquid evaporated gives a residue of hydrochlorates of alkaloids. The latter will afford characteristic reactions with the tests for the suspected alkaloid, and, on being moistened with baryta-water and warmed, will afford fumes of volatile alkaloids whose odor is usually characteristic. The residue in the flask will contain non-volatile alkaloids. It is treated with carbonic acid gas to neutralize and precipitate the excess of baryta as insoluble carbonate of barium; the mixture is evaporated to dryness over a water-bath, and the residue digested in alcohol. The alcoholic solution evaporated generally yields the alkaloids in a fit state for testing.

Reagents for Alkaloids.

Phosphomolybdic acid forms with ammonia, in acid solutions, a remarkably insoluble compound, and it comports itself in a similar manner with those compounds which are analogous to ammonia, the nitrogenized organic bases; consequently forming an excellent reagent for their detection. It may be prepared in the following manner: Molybdate of ammonium is precipitated by phosphate of sodium; the yellow precipitate, having been washed, is diffused through water, and heated with sufficient carbonate of sodium to dissolve it. The solution is then evaporated to dryness, and calcined to drive off the ammonia. In case any of the molybdic compound be reduced by this operation, the residue must be moistened with nitric acid and again calcined. The dry mass is then dissolved in cold water, the solution strongly acidulated with nitric acid, and water added until 10 parts of the solution contain 1 of the dry salt. The liquid, which is of a golden-yellow color, must be preserved from ammoniacal fumes. It precipitates all the alkaloids (with the exception of urea) when a mere trace only is present. The precipitates are yellow, generally flocculent, insoluble in water, alcohol, ether, and the dilute mineral acids, with the exception of phosphoric acid. Nitric, acetic, and oxalic acids, concentrated and boiling, dissolve them. These compounds are decomposed by the alkalies, certain metallic oxides, and the alkaline salts, which separate the alkaloid. To give an idea of the sensitiveness of this reagent, it may be stated that the 0.000071 gramme of strychnine gives an appreciable precipitate with one cubic centimetre of the solution of phosphomolybdic acid.

Phosphoantimonic acid and phosphotungstic acid are also precipitants of alkaloids. The chlorides of platinum, iridium, palladium, and gold are occasionally serviceable. Tannic acid and picric acid may too be used.

Other special reagents for alkaloids are the "Nessler test" (see Index), the double iodide of potassium and cadmium, and a solution of the double "Iodide of Bismuth and Potassium." The latter is made (by Thresh) on adding together 1 ounce of *Liquor Bismuthi*, B. P., 90 grains of iodide of potassium, and 90 grains of strong hydrochloric acid. This orange-colored solution gives a red precipitate with dilute cold solutions containing alkaloids.

Obscure Poisons.—Many substances, the active principles of which are at present beyond the reach of the chemical analyst, are poisons of a more or less active character. (See the *Pharmaceutical Journal* for Sept. 6, 1879, p. 195, and for Dec. 20, 1879, p. 481.)

Ptomaines are poisonous alkaloids producible from the human body itself after death during the ordinary processes of decay. But they are distinguished, according to Bronardel and Boutmy, by a drop or two of a solution of their sulphate converting a drop of solution of ferrocyanide of potassium into ferridcyanide, the mixture then giving a dark-blue precipitate with a ferric salt. Unfortunately, some other substances possess this converting power.

ANTIDOTES.

Vide "Antidote" in the Index.

QUESTIONS AND EXERCISES.

878. In examining food and similar matter for poison, why must not the ordinary tests for the poison be at once applied?

879. What preliminary operations should be performed on a vomit in a case of suspected poisoning?

880. How would you proceed in searching for corrosive sublimate in wine?

881. By what series of operations would you satisfy yourself of the presence or absence of arsenic in the contents of a stomach?

882. Describe the treatment to which decoction of coffee should be subjected in testing it for tartar-emetic.

883. State the method by which the occurrence of lead in water is demonstrated.

884. Give a process for the detection of copper in jam.

885. How would you detect zinc in a vomit?

886. How may the presence of a poisonous quantity of sulphuric acid in gin be proved?

887. In examining ale for free nitric acid what reactions would be selected?

888. Show how you would conclude that a dangerous quantity of hydrochloric acid had been added to cider.

889. Describe the manipulations necessary in testing for hydrocyanic acid in the contents of a stomach.

890. By what method is oxalic acid discovered in infusion of coffee?

891. How is the phosphorus detected in organic mixtures?

892. Give the process by which strychnine is isolated from partially digested food.

893. Mention the experiments by which the presence of laudanum in porter is demonstrated.

894. Name the appropriate antidotes in cases of poisoning by—*a*, alkaloids; *b*, antimonials; *c*, arsenic; *d*, barium salts; *e*, copper compounds; *f*, hydrochloric acid; *g*, hydrocyanic acid; *h*, preparations of lead; *i*, corrosive sublimate; *j*, nitric acid; *k*, oxalic acid; *l*, salts of silver; *m*, oil of vitriol; *n*, tin liquors; *o*, zinc solutions; *p*, carbolic acid.

EXAMINATION OF MORBID URINE AND CALCULI.

The various products of the natural and continuous decay of animal tissue and the refuse matter of food are eliminated from the system chiefly as fæces, urine, and expired air. Air exhaled from the lungs carries off from the blood much carbon (about 8 ounces in twenty-four hours) in the form of carbonic acid gas and some aqueous vapor—the latter, together with a small amount of oily matter, also escaping by the skin. Directing the breath to a cold surface renders moisture evident, and breathing through a tube into lime-water demonstrates the presence of a considerable quantity of carbonic acid gas. The fæces consist mainly of the insoluble *débris* of the system, the soluble matters and water forming the urine. These excretions vary considerably according to the food and general habits of the individual and external temperature. But in disease the variations become excessive; their detection by the medical practitioner, or by the pharmacist for the medical practitioner, is therefore a matter of importance.

A complete analysis of fæces, urine, or expired air cannot be performed in the present state of our knowledge. Nor can even a partial analysis of fæces or air be made with sufficient ease and rapidity to be practically available in medical diagnosis. But with regard to urine, certain abnormal substances and abnormal quantities of normal constituents may be chemically detected in the course of a few minutes by any one having already some knowledge of chemical manipulation.

Healthy human urine contains, in 1000 parts, 957 of water, 14 of urea, 1 of uric acid, 15 of other organic matter, and 13 of inorganic salts. The amount passed in twenty-four hours varies from two to three pints in an adult, and its specific gravity, if healthy, will range from 1.015 to 1.025. The acidity of urine Thudichum considers to be due to *cryptophanic acid*, $H_2C_5H_7NO_5$.

EXAMINATION OF MORBID URINE FOR ALBUMEN, SUGAR, BILE, AND EXCESS OF UREA; AND URINARY SEDIMENT FOR URATES (OR LITHATES), PHOSPHATES, OXALATE OF CALCIUM, AND URIC ACID.

Albumen.—To detect albumen, acidulate a portion of the clear urine in a test-tube with a few drops of acid (to keep phosphates in solution—nitric is best, acetic not so good), and boil; flocks or coagula will separate if albumen be present.

This experiment should first be made on normal urine containing a drop or two of solution of white of egg. The coagulum is white if it is only albumen, greenish if bile-pigment be present, and brownish-red if the urine contain blood. The influence of acids and alkalies on the precipitation of albumen is noticed on page 456.

The occurrence of albumen in the urine may be temporary and of but little importance, or it may indicate the existence of a serious affection known as Bright's disease.

Sugar.—To a portion of the clear urine in a test-tube add five or ten drops of solution of sulphate of copper; pour in solution of potash or soda until the precipitate first formed is redissolved; slowly heat the solution to near the boiling-point; a yellow, yellowish-red, or red precipitate (cuprous oxide) is formed if sugar be present.

This experiment should first be made on urine containing a drop or two of solution of grape-sugar (page 411). The hydrate of copper precipitated by the alkali is insoluble in excess of pure potash or soda, but readily dissolves if organic matter, especially sugar, be present. The copper salt may not contain iron.

Other tests may be applied if necessary (*vide* pages 411 *et seq.*)

A minute amount of sugar is said to occur in normal urine, and a distinct trace is occasionally present. In larger quantities (often 5 per cent.) it is a characteristic constituent of the urine of diabetic patients, greatly increasing the specific gravity of the excretion. Small hydrometers (termed urinometers) are commonly employed for quickly and readily ascertaining the specific gravity of urine;

they range from 1.000 to 1.050, the interval of 1.015 to 1.025 being marked as "H. S." or healthy state. (*Vide* "Specific Gravity" and "Hydrometers" in Index.)

Bile.—This is best detected by the general test (Pettenkofer's, or, still better, Quinlan's) described on page 464. Or a little of the urine may be placed on a white plate, and strong nitric acid dropped on it; a peculiar play of colors—green, yellow, violet, etc.—occurs if (the coloring-matter of) bile be present (Gmelin). A somewhat similar iridescence is produced in the presence of the indigo-forming matter occasionally found in urine.

Excess of Urea.—About one-third of the solid matter in the urine is urea. Its proportion varies considerably, but 1½ per cent. may be regarded as an average amount. Concentrate urine slightly by evaporation in a small dish, pour the liquid into the test-tube, set the tube aside till cold, or cool it by letting cold water run over the outside; add an equal bulk of strong nitric acid and again set aside; scaly crystals of nitrate of urea are deposited more or less quickly.

With regard to the amount of urea in urine it is impossible to sharply define excess or deficiency. If nitric acid gives crystals without concentration, excess is certainly present. A rough estimate may be formed by mixing a few drops of the urine and acid on a piece of glass and setting aside; the time which elapses before crystals form is an indication of the quantity in the specimen. The time will vary according to the temperature and state of moisture of the atmosphere, but with care some useful comparative results may in this way be obtained.

For methods of estimating the amount of urea in urine, and for drawings of the necessary apparatus, *vide Journal of the Chemical Society*, 1874, p. 749; and 1877, i. pp. 534 and 538; also *Chemical News*, Jan. 22, 1875.

Tests.—Urea in solution in water may be detected by the above reaction with nitric acid and by the readiness with which it yields ammonia on being boiled with alkalies. In putrid urine its conversion into an ammoniacal salt has already been effected by ammoniacal fermentation.

$$\underset{\text{Urea.}}{CH_4N_2O} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carbonate of ammonium.}}{(NH_4)_2CO_3}.$$

This transformation of the urea into carbonate of ammonium is due to the action of a special ferment belonging to the genus *Torulacei*, formed of chaplets of globules similar in form to, but much smaller than, those of beer-yeast. It occurs as a white deposit in the urine. If some of this deposit be added to a saccharine solution containing urea, it rapidly multiplies, carbonate of ammonium being formed.

Formula of Urea.—The empirical formula of urea is CH_4N_2O. Its rational formula may be thus written:— $\left.\begin{array}{r}(CO)''\\ H_2\\ H_2\end{array}\right\}N_2$; that is, it may be regarded as one of the organic bases already referred to, a primary diamine, in which the bivalent radical CO occupies the place of H_2. The other atoms of hydrogen may be displaced by various radicals, and many *compound ureas* thus be obtained.

Artificial Urea.—Urea may be prepared artificially by Williams's modification of Wöhler's method. Cyanide of potassium of the best commercial quality (containing about 90 per cent. of real cyanide) is fused at a very low red heat in a shallow iron vessel; red lead is added in small quantities at a time, the temperature being kept down by constant stirring. When the red lead ceases to cause further action, the mixture (cyanate of potassium and lead) is allowed to cool, the product finely powdered, exhausted with cold water, nitrate of barium added till no more precipitate (carbonate of barium) falls, the mixture filtered, and the filtrate treated with nitrate of lead so long as cyanate of lead is thrown down. The latter is thoroughly washed, and dried at a low temperatnre. Equivalent quantities of cyanate of lead and sulphate of ammonium, digested in a small quantity of water at a gentle heat and filtered, yield a solution from which urea crystallizes on cooling.

Another Process.—Basaroff has found that urea is produced when ordinary carbonate of ammonium is heated in hermetically sealed tubes to about 275° F. for a few hours. The same chemist had previously obtained urea by similarly heating pure carbonate of ammonium, so that the source of the urea in the former case is probably the carbamate of ammonium believed to occur in the carbonate (see p. 91).

$$NH_4NH_2CO_2 - H_2O = CH_4N_2O.$$

Notes.—Urinary deposits are seldom of a complex character; the action of heat and acetic and hydrochloric acids generally at once indicates the character of the deposit, rendering filtration and precipitation unnecessary.

The urates are often of a pink or red color, owing to the presence of a pigment termed *purpurine;* hence the common name of *red gravel* for such deposits. *Purpurine* is soluble in alchol, and may be removed by digesting a red deposit in that solvent. It is seldom necessary to determine whether the urate be that of ammonium, calcium, or sodium (see also Uric Acid, p. 357).

The *phosphate of calcium* and the *ammonio-magnesium phosphate* are usually both present in a phosphatic deposit, the magnesium salt forming the larger proportion. They may, if necessary and if sufficient in quantity, be separated by collecting on a filter, washing, and boiling with solution of carbonate of sodium. The carbonates of calcium and magnesinm thus formed are collected on a filter, washed, and dissolved in a drop or two of hydrochloric acid; chloride of ammonium, ammonia, and carbonate of ammonium are added, and the mixture boiled and filtered; any calcium originally present will then remain insoluble as carbonate of calcium, while any magnesium will be precipitated from the filtrate as ammonio-magnesium phosphate on the addition of phosphate of sodium, the mixture being also well stirred.——The chief portion of excreted phosphates is carried off by the fæces, that remaining in the urine being kept in solution by the influence of acid phosphate of sodium, and frequently lactic acid.——Occasionally, an hour or two after a hearty meal, the urine becomes sufficiently alkaline for the phosphates to be deposited, and the urine when passed is turbid from their presence.——The ammoniacal constituent of the magnesium salt does not occur normally, but is produced from urea as soon as urine becomes alkaline.

URINARY SEDIMENTS.

Warm the sediment with the supernatant urine and filter.

<table>
<tr><td colspan="3"><i>Insoluble.</i>
Phosphates, oxalate of calcium, and uric acid.
Warm with acetic acid, and filter.</td><td rowspan="3"><i>Soluble.</i>
Urates—of ammonium, calcium, or sodium, chiefly the latter.
They are redeposited as the liquid cools, and if sufficient in quantity may be further examined for ammonium, calcium, sodium, and the uric radical by the appropriate tests.</td></tr>
<tr><td colspan="2"><i>Insoluble.</i>
Oxalate of calcium and uric acid.
Warm with hydrochloric acid, filter.</td><td rowspan="2"><i>Soluble.</i>
Phosphates.
Add ammonia, white ppt. = phosphate of calcium, or ammonio-magnesium phosphate, or both.</td></tr>
<tr><td><i>Insoluble.</i>
Uric acid.
Apply murexid test (p. 358).</td><td><i>Soluble.</i>
Oxalate of calcium.
May be precipitated by ammonia.</td></tr>
</table>

Oxalate of calcium is seldom met with in excessive amounts, but very often in small quantities mixed with phosphates.

In one case of oxaluria the whole urine excreted by a patient in twenty-four hours furnished to the author only two-thirds of a grain of oxalate of calcium.

Free uric acid is in most cases distinctly crystalline, and nearly always of a yellow, red, or brown color.

Artificial Sediments.—For educational practice artificial deposits may be obtained as follows:—1. Rub up in a mortar a few grains of serpent's excrement (chiefly urate of ammonium) with an ounce or two of urine; this represents a sediment of urates. 2. Add a few drops of solution of chloride of calcium and of phosphate of sodium to urine; the deposit may be regarded as one of phosphates. 3. To an ounce or two of urine add very small quantities of chloride of calcium and oxalate of ammonium; the precipitate is oxalate of calcium. 4. To urine acidulated by hydrochloric acid add a little serpent's excrement; the sediment is uric acid.

Other deposits than the foregoing are occasionally observed. Thus *hippuric acid* ($HC_9H_8NO_3$), a normal constituent of human urine, and largely contained in the urine of herbivorous animals, is sometimes found associated with uric acid in urinary sediment, especially in that of patients whose medicine contains benzoic acid (p. 333). Its appearance, as observed by the aid of the microscope, is characteristic—namely, slender, four-sided prisms, having pointed ends. *Cystin* ($C_3H_7HSO_2$) (from *κὺστις*, *kūstis*, a bladder, in allusion to its origin) rarely occurs as a deposit in urine. It is not soluble in warm urine or dilute acetic acid, and scarcely in dilute hydrochloric acid, hence would be met with in testing for free uric acid. It is very soluble in ammonia, recrystallizing from a drop of the solution placed on a piece of glass in characteristic microscopic six-sided plates. *Organized sediments* may be due to the corpuscles of pus, mucus, or blood, fat-globules, spermatozoa, cylindrical casts of the tubes of the kidneys, epithelial cells from the walls of the bladder, or foreign matters, such as fibres of wood, cotton, small feathers, dust, starch; these are best recognized by the microscope, as will be seen by the following paragraphs and figures on the microscopic appearances of both crystalline and organized urinary sediments.

MICROSCOPIC EXAMINATION OF URINARY SEDIMENTS.

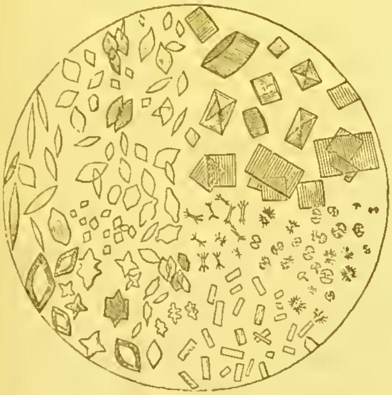
Urine containing insoluble matter is usually more or less opaque. For a microscopical examination a few ounces should be set aside in a conical test-glass for an hour or two, the clear supernatant urine poured off from the sediment as far as possible, a small drop of the residue placed on a slip of glass and covered with a piece of thin glass, and examined under the microscope with different magnifying powers.

[The respective appearances of the various crystalline and organized matters are given in the following figures, which were kindly drawn by H. B. Brady, F. R. S., from natural specimens (as seen with a two-third inch objective and No. 1 eye-piece—*i. e.*, magnified 60 diameters) in the collections of St. Bartholomew's Hospital, Dr. Sedgwick, W. W. Stoddart, F. C. S., Mr. Waddington, and the author.]

Uric Acid occurs in many forms, most of which are given in the first two figures. Flat, more or less oval crystals, sometimes attached to each other, their outline then resembling an 8, a cross, or a star, are common. Single and grouped quadratic prisms, aigrettes, spicula, and crystals recalling dumb-bells are met with. From urine acidulated by hydrochloric acid square crystals, two opposite sides smooth and two jagged, are generally deposited; acidulated by acetic acid, more typical forms are obtained. A drop of solution of potash or soda placed on a glass slip will dissolve a deposit of uric acid, a drop of any acid reprecipitating it in minute but characteristic crystals.

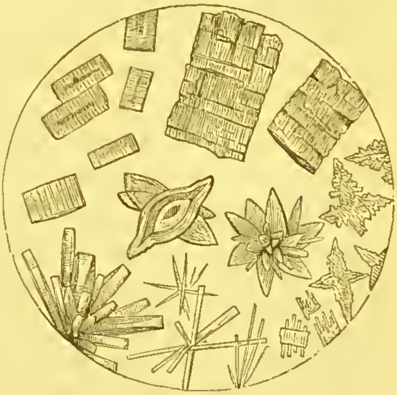
Cystin is very rarely met with as a urinary deposit; that from which the figure was taken was found in the urine of a patient in St. Bartholomew's Hospital. Lamellæ of cystin always assume an hexagonal character, but the angles are sometimes ill defined and the plates superposed; in the latter case, a drop of solution of ammonia placed on the glass at once dissolves the deposit, well-marked six-sided crystals appearing as the drop dries up.

Fig. 50.



Uric Acid.

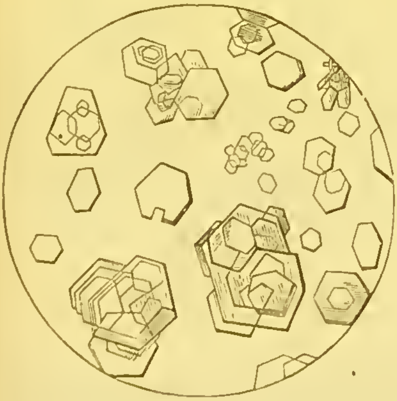
Fig. 51.



Uric Acid.

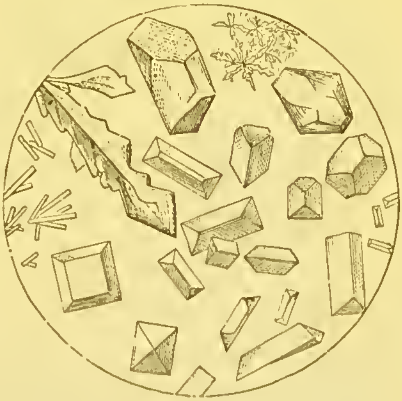
Triple Phosphate (phosphate of magnesium and ammonium) is deposited as soon as urine becomes alkaline, the ammoniacal constituent being furnished by the decomposition of urea. It occurs in large prismatic crystals, forming a beautiful object when viewed by polarized light; sometimes also in ragged stellate or arborescent crystals resembling those of snow. Both forms may be artificially

Fig. 52.



Cystin.

Fig. 53.



Triple Phosphate.

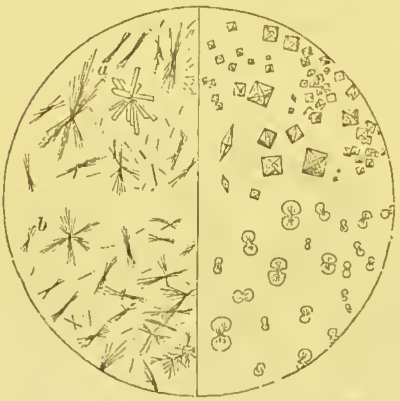
prepared by adding a small lump of carbonate of ammonium to a few ounces of urine and setting aside in a test-glass.

Amorphous deposits are either *earthy phosphates* (a mixture of phosphates of magnesium and calcium) or *urates* (of calcium, magnesium, ammonium, potassium, or sodium—chiefly the latter). They may be distinguished by the action of a drop of acetic acid placed near the sediment on the glass slip, the effect being watched under the microscope; phosphates dissolve, while urates gradually assume characteristic forms of uric acid. Urates redissolve when warmed with the supernatant urine.

Urates of Sodium and Magnesium, though generally amorphous, occasionally take a crystalline form—bundles or tufts of small needles—as shown in the cut.

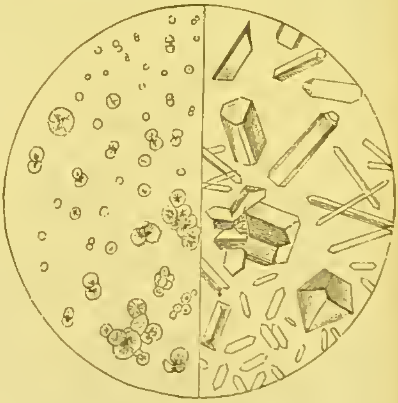
Oxalate of Calcium commonly occurs in octahedra requiring high magnifying-power for their detection. The crystals are easily overlooked if other matters are present, but are more distinctly seen after phosphates have been removed by acetic acid. In certain aspects the smaller crystals look like square plates traversed by a cross. A dumb-bell form of this deposit is also sometimes seen, resembling certain forms of uric acid and the coalescing spherules of a much rarer sediment, carbonate of calcium. Oxalate of calcium is insoluble in acetic, but soluble in hydrochloric, acid. The octahedra are frequently met with in the urine of persons who have partaken of garden rhubarb; the crystals may often be deposited artificially (according to Waddington) by dropping a fragment of oxalic acid into several ounces of urine and setting aside for several hours.

Fig. 54.



Urates. a, of Sodium; b, of Magnesium. | Oxalate of Calcium.

Fig. 55.



Carbonate of Calcium. | Hippuric Acid.

Carbonate of Calcium is rarely found in the urine of man, but frequently in that of the horse and other herbivorous animals. Human urine containing carbonate of calcium often reddens litmus-paper; and it is only after the removal, on standing, of the excess of carbonic acid that the salt is deposited. It consists of minute spherules, varying in size, the smaller ones often in process of coalescence.

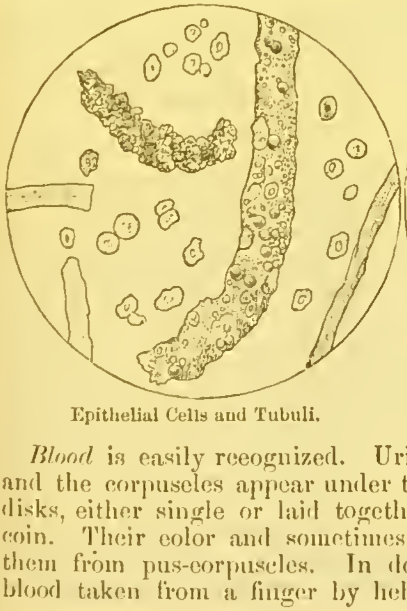
The dumb-bell form thus produced is easily distinguished from similar groups of uric acid or oxalate of calcium by showing a black cross in each spherule when viewed by polarized light. Acetic acid dissolves carbonate of calcium, liberating carbonic acid gas, with visible effervescence (under the microscope) if the slide has been previously warmed and a group of crystals be attacked.

Hippuric Acid.—The pointed rhombic prisms and acicular crystals are characteristic and easily recognized. The broader crystals may possibly be mistaken for triple phosphate, and the narrower for certain forms of uric acid; but insolubility in acetic acid distinguishes them from the former, and solubility in alcohol from the latter. These tests may be applied while the deposit is under microscopic observation. An alcoholic solution of hippuric acid evaporated to dryness, and the residue treated with water, gives a solution from which characteristic crystalline forms of hippuric acid may be obtained on allowing a drop to dry upon a slip of glass.

The organized deposits in urine entail greater care in their determination, and usually require a higher magnifying-power for their proper examination, than those of crystalline form. The figures are drawn to 230 diameters. The following notes will assist the observer:—

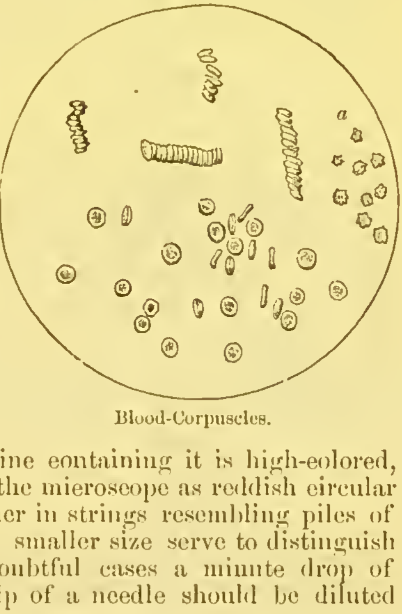
Casts of uriniferous tubuli are fibrinous masses of various forms, and often of considerable length—sometimes delicate and transparent, occasionally granular, and often beset with fat-globules. Epithelial *débris* are frequently present in urine in the form of nucleated cells, regular and oval when full, but angular and unsymmetrical when partially emptied of their contents—sometimes perfect, but more frequently a good deal broken up.

Fig. 56.



Epithelial Cells and Tubuli.

Fig. 57.

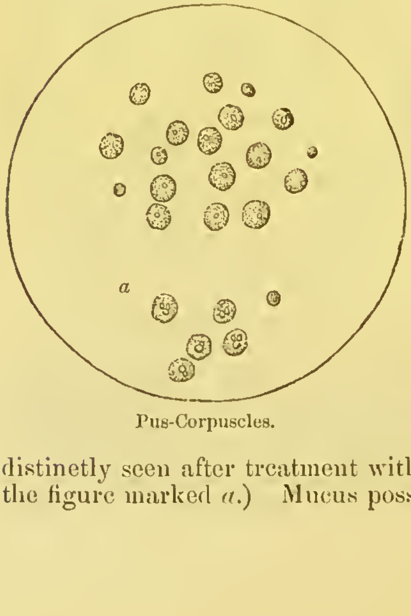


Blood-Corpuscles.

Blood is easily recognized. Urine containing it is high-colored, and the corpuscles appear under the microscope as reddish circular disks, either single or laid together in strings resembling piles of coin. Their color and sometimes smaller size serve to distinguish them from pus-corpuscles. In doubtful cases a minute drop of blood taken from a finger by help of a needle should be diluted with water and used for comparison. After urine containing blood has stood for some time the corpuscles lose their regular outline and become angular. (See *a* in the figure.) Day, of Geelong, tests for blood in urine or in stains on clothing by adding a few drops of a recently-prepared alcoholic solution of the inner unoxidized portions of guaiacum resin, and then a small quantity of Robbins's aqueous or ethereal solution of peroxide of hydrogen, when a blue color results. "If the stain is on a dark-colored fabric, the moistened parts may be pressed with white blotting-paper, when blue impressions will be obtained. Contact with many substances causes the blue reaction or oxidation of guaiacum; the peculiarity of blood is that it does not produce this effect unless peroxide of hydrogen or a similar 'antozonic' liquid is present. Bodies such as permanganate of potassium, whose oxygen is, apparently, in the form of ozone, also give rise to a blue color with guaiacum; peroxide of hydrogen and other compounds whose oxygen is in the opposite, positive, or, according to Schönbein, antagonistic condition, produce no such effect. It would seem as if blood or some other constituent of blood has the power of converting positive into negative oxygen, and thus bring about an effect which negative oxygen alone is able to produce; for of all substances which, like blood, do not alone cause guaiacum to become blue, blood is the only one that so affects 'antozonides' (themselves inactive) as to enable them to act as ozonides—that is, to oxidize the guaiacum. Both the venous and arterial fluid from any red-blooded animal will produce this blue reaction. Fruit-stains are darkened by ammonia, which does not alter the color of blood. Iron-stains or iron-mould yields no color to water, whereas the red coloring-matter of blood is soluble in water. The peroxide of hydrogen should be free from more than a trace of acid."

The blood-corpuscles of ordinary animals are much smaller than those of man, but a $\frac{1}{16}$ or $\frac{1}{25}$ of an inch lens is necessary for proper differentiation (J. G. Richardson).

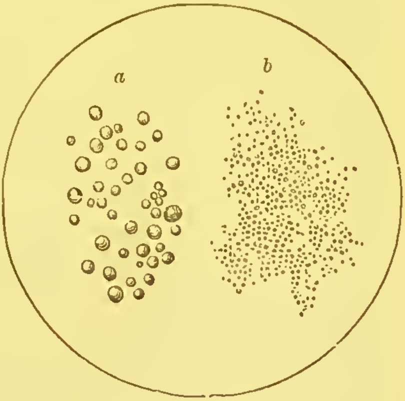
Fig. 58.



Pus-Corpuscles.

Pus and Mucus.—Purulent urine deposits, on standing, a light-colored layer, easily diffused through the liquid by shaking. Acetic acid does not dissolve the sediment, and solution of potash, of official strength, converts it into a gelatinous mass. Under the microscope, pus-corpuscles appear rounded and colorless, rather larger than blood-disks, and somewhat granular on the surface. They generally show minute nuclei, which are more distinctly seen after treatment with acetic acid. (See the portion of the figure marked *a*.) Mucus possesses no definite microscopic characters, but commonly has imbedded in it pus, epithelium, and air-bubbles. Mucus is coagulated in a peculiar and characteristic manner by acetic acid; and this reaction, together with the ropy appearance it imparts to urine, prevents its being confounded with pus. Day's test for pus consists in adding a drop or two of oxidized tincture of guaiacum to the urine or other liquid, when a clear blue color is produced. It is necessary to moisten dry pus with water before applying the test. The test-liquid is made by exposing a saturated alcoholic solution of guaiacum to the air until it has absorbed a sufficient quantity of oxygen to give it the property of turning green when placed in contact with iodide of potassium. Day's test for mucus consists in the application, first, of oxidized tincture of guaiacum, which by itself undergoes no change in the presence of mucus, and then in the addition of carbolic acid or creasote, which quickly changes the color of the guaiacum to a bright blue. Neither carbolic acid nor creasote alone will render guaiacum blue. In testing for mucus on cloths or when it is mixed with blood, it is necessary to use the carbolic acid pure, but when the mucus is in a liquid state it is better to use carbolic acid diluted with alcohol.

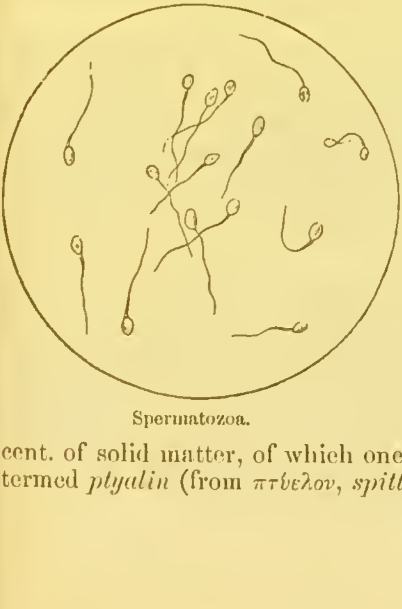
Fig. 59.



Fat-Globules.

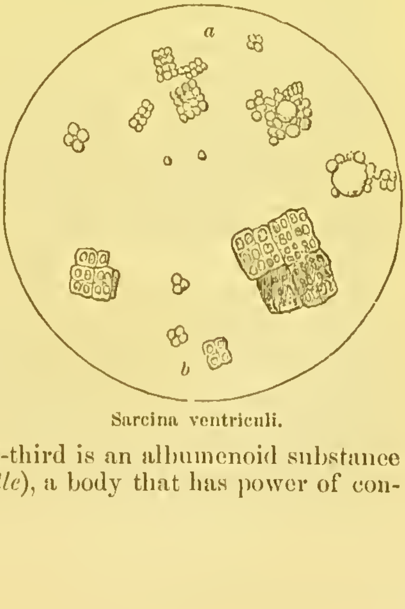
Saliva.—Saliva is an aqueous fluid containing less than 1 per cent. of solid matter, of which one-third is an albumenoid substance termed *ptyalin* (from πτύελον, *spittle*), a body that has power of con-

Fig. 60.



Spermatozoa.

Fig. 61.



Sarcina ventriculi.

verting starch into dextrin and grape-sugar. Alkaline salts, including a trace of sulphocyanate of potassium, and calcareous compounds are also present.

Day's test for saliva in urine, etc. is similar to that for mucus, with the exception that the blue reaction produced by the oxidized tincture of guaiacum and alcoholic solution of carbolic acid is highly intensified by the addition of Robbins's aqueous or ethereal solution of peroxide of hydrogen.

Fatty matter occurs either as minute globules partially diffused through the urine (as shown at *a*, Fig. 59) or in more intimate emulsion (as at *b*). When present in larger quantity it collects as a sort of scum on the surface after standing.

Spermatozoa are liable to escape notice on account of their small size and extreme transparency. Suspected urine should be allowed to settle some hours in a conical test-glass, and the drop at the bottom examined under a high power. The drawing (Fig. 60) shows their tadpole-like appearance.

Sarcina ventriculi is an alga of a very rare occurrence in urine, though not unfrequent in the matters vomited during certain diseases of the stomach. The upper figures (*a*, Fig. 61) are copied from Dr. Thudichum's drawing (from urine); the larger fronds (*b*) are from vomited matter.

Extraneous bodies, such as hair, wool, or fragments of feathers, are often found in urinary deposits, and ludicrous mistakes have been made by observers not on their guard in respect to such casual admixtures.

EXAMINATION OF URINARY CALCULI.

The term *calculus* is the diminutive of *calx*, a lime- or chalk-stone.

Knowledge of the composition of a calculus or urinary deposit affords valuable diagnostic aid to the physician; hence the importance of a correct analysis of these substances.

Nature of Calculi.—Urinary calculi have the same composition as unorganized urinary sediments. They consist, in short, of sediments that have been deposited slowly within the bladder, particle on particle, layer on layer, the several substances becoming so compact as to be less easily acted on by reagents than when deposited after the urine has been passed—the urates less readily soluble in warm water, the calcic phosphate insoluble in acetic acid until it has been dissolved in hydrochloric acid and reprecipitated by an alkali.

Preliminary Treatment.—If the calculus is whole, saw it in two through the centre, and notice whether it is built up of distinct layers or apparently consists of one substance. If the latter, use about a grain of the sawdust for the analysis; if the former, carefully scrape off portions of each layer and examine them separately. If the calculus is in fragments, select fair specimens of about half a grain or a grain each, and reduce to a fine powder by placing on a hard surface and crushing under the blade of a knife.

Analysis.—Commence the analysis by heating a portion, about the size of a pin's head, on platinum foil, in order to ascertain whether organic matter, inorganic matter, or both are present. If both, the ash is examined for inorganic substances, and a fresh portion of the calculus for uric acid by the murexid test. (In the absence of uric acid any slight charring may be considered to be due to indefinite animal matter.) If composed of organic matter only, the calculus will in nearly all cases be uric acid, the indications being confirmed by applying the murexid test, in a watch-glass, to another fragment half the size of a small pin's head. If inorganic only, the ash on the platinum foil may be examined for phosphates, and a separate portion of the calculus for oxalates. Even a single drop of liquid obtained in any of these experiments may be filtered by placing it on a filter not larger than a sixpence and previously moistened with water, and adding three or four drops of water one after the other as each passes through the paper. If the calculus is suspected to contain more than one substance, boil about half a grain of the powder in half a test-tubeful of distilled water for a few minutes, and pour it on a small filter; then proceed according to the following Table:—

<table>
<tr>
<td colspan="3"><i>Insoluble.</i>
Phosphates, oxalate of calcium, and free uric acid.
Boil with two or three drops of hydrochloric acid, and filter.</td>
<td rowspan="3"><i>Soluble.</i>
Urates.
These will probably be redeposited as the solution cools. Small quantities may be detected by evaporating the solution to dryness. They are tested for ammonium, sodium, calcium, and the uric radical by the appropriate reagents.</td>
</tr>
<tr>
<td rowspan="2"><i>Insoluble.</i>
Uric acid. Apply the murexid test (p. 358).</td>
<td colspan="2"><i>Soluble.</i>
Phosphates and oxalate of calcium.
Add excess of ammonia, and then excess of acetic acid; filter.</td>
</tr>
<tr>
<td><i>Insoluble.</i>
Oxalate of calcium.</td>
<td><i>Soluble.</i>
Phosphates.
They may be reprecipitated by ammonia.</td>
</tr>
</table>

Varieties of Calculi.—Calculi composed entirely of *uric acid* are common; a minute portion heated on platinum foil chars, burns, and leaves scarcely a trace of ash. The phosphates frequently occur together, forming what is known as the *fusible calculus* from the readiness with which a fragment aggregates, and even fuses to a bead, when heated on a loop of platinum wire in the blowpipe-flame. The phosphates may, if necessary, be further examined by the method described in connection with urinary deposits. Oxalate of calcium often occurs alone, forming a dark-colored calculus having a very rough surface, hence termed the *mulberry calculus.* Smaller calculi of the same substance are called, from their appearance, *hempseed calculi.* Calculi of *cystin* are rarely met with. *Xanthin* (from ξανθὸς, *xanthos*, yellow, in allusion to the color it yields with nitric acid) less often occurs as a calculus. The earthy concretions, or *chalk-stones*, which frequently form in the joints of gouty persons are composed chiefly of urates, the sodium salt being that most commonly met with. *Gall-stones*, or *biliary calculi*, occasionally form in the gall-bladder; they contain *cholesterin* (from χολή, *cholē*, bile, and στερεὸς, *stereos*, solid), a fatty substance of alcoholoid constitution, soluble in rectified spirit or ether, and crystallizing from such solutions in well-defined, square, scaly crystals. Phosphatic and other calculi of many pounds weight are occasionally found in the stomach and larger intestines of animals.

QUESTIONS AND EXERCISES.

895. In breathing, how much carbon (in the form of carbonic acid gas) is exhaled from the lungs every 24 hours?

896. How may the presence of carbonic acid gas in expired air be demonstrated?

897. Mention an experiment showing the escape of moisture from the lungs during breathing.

898. State the method of testing for albumen in urine.

899. Give the tests for sugar in urine.

900. What is the average composition of healthy urine?

901. Give the tests for urea.

902. Write the rational formulæ of some compound ureas in which methyl or ethyl displaces hydrogen.

903. Describe an artificial process for the production of urea, giving equations.

904. Sketch out a plan for the chemical examination of urinary sediments.

905. A deposit is insoluble in the supernatant urine or in acetic acid; of what substance may it consist?

906. Which compounds are indicated when a deposit redissolves on warming it with the supernatant urine?

907. Name the salts insoluble in warmed urine, but dissolved on the addition of acetic acid.

908. Mention the chemical characters of cystin. At what stage of analysis would it be recognized?

909. Describe the microscopical appearance of the following urinary deposits:—

Uric acid.
Cystin.
Triple phosphate.
Earthy phosphates.
Urates.
Oxalate of Calcium.
Carbonate of Calcium.
Hippuric Acid.
Tube-casts.
Epithelial *débris*.
Blood.
Pus.
Mucus.
Fat.
Spermatozoa.
Sarcina.
Extraneous Bodies.

910 How are Day's tests for blood, pus, and saliva applied?

911. What is the general, physical, and chemical nature of urinary calculi?

912. How are urinary calculi prepared for chemical examination?

913. Draw out a chart for the chemical examination of urinary calculi.

914. Why is the "fusible calculus" so called? and what is its composition?

915. State the characters of "mulberry" and "hempseed" calculi.

916. What are the "chalk-stones" of gout, and "gall-stones" or "biliary calculi"?

THE GALENICAL PREPARATIONS OF THE PHARMACOPŒIAS.

The preparation of Abstracts, Cerates, Confections, Decoctions, Elixirs, Enemas, Extracts, Glycerins, Infusions, Inhalations, Juices, Liniments, Lozenges or Troches, Mixtures, Ointments, Pills, Plasters, Poultices, Powders, Spirits, Suppositories, Syrups, Tinctures, Triturations, and Wines includes a number of mechanical rather than chemical operations, and belongs to the domain of pure Pharmacy. The medical or pharmaceutical pupil will have had ample opportunity of practically studying those compounds before working at experimental chemistry, and will probably have prepared many of them according to the directions of the Pharmacopœias; if not, he is referred to the pages of the last edition of those works for details.

Among the extracts of the British Pharmacopœia, however, there are five (namely, those of Aconite, Belladonna, Hemlock, Henbane, and Lettuce) which are not simply evaporated infusions, decoctions, or tinctures, like most others, but are evaporated juices from which vegetable albumen, the supposed source of fermentation and decay, has been removed, and chlorophyll (the green coloring-mater of plant-juice) retained, practically unimpaired in tint. For educational practice either of the above-named five raw materials may be employed; but in order that attention may be concentrated on the process by which the extracts are prepared, rather than on any one of the extracts themselves, it suffices to make an extract of some ordinary green vegetable, such as cabbage or turnip-tops. Bruise the green leaves of a good-sized cabbage in a mortar, and press out the juice: heat it gradually to 130° F., and remove the green flocks of chlorophyll which separate, by filtration through calico. When the liquor has all passed through the filter, set the chlorophyll aside for a time, heat the strained liquor to 200° F. to coagulate albumen; remove the latter by filtration and throw it away; evaporate the filtrate by a water-bath to the consistence of thin syrup; then add to it the chlorophyll, and, stirring the whole together assiduously, continue the evaporation at a temperature not exceeding 140° F. until the extract is of a suitable consistence for forming pills. A higher temperature than that indicated would cause the alteration of the chlorophyll to a dark-brown substance, any such extract used in pharmacy no longer having the green tint which custom and the British Pharmacopœia demand.

QUESTIONS AND EXERCISES.

917. Enumerate the different classes into which official galenical preparations may be divided.

918. Describe the general process for the preparation of green extracts:—

Aconite. Hemlock.
Belladonna. Henbane.
Lettuce.

919. Why is vegetable albumen excluded in the preparation of green extracts?

920. How may chlorophyll be removed from vegetable juices, and again be introduced into their evaporated residues, without destroying its color?

921. For what reason is exposure of chlorophyll to a boiling temperature avoided in the manufacture of green extracts?

THE CHEMICAL PREPARATIONS OF THE PHARMACOPŒIAS.

The process by which every official chemical substance is prepared has already been described, and the strict chemical character of the processes illustrated by experiments and explained by aid of equations. Should the reader, in addition, desire an intimate acquaintance with those details of manipulation on which the successful and economic manufacture of chemical substances depends, he is advised to prepare, if he has not done so already, a few ounces of each of the salts mentioned in the Pharmacopœias or commonly used in Pharmacy. An additional guide in these operations will be the Pharmacopœia itself.

The production of many chemical and galenical substances on a commercial scale can only be successfully carried on in manufacturing laboratories and with some knowledge of the circumstances of supply and demand, value of raw material and of by-products, etc.; for the technical preparation of such substances requires much knowledge beyond even a thorough acquaintance with Chemistry. Still, in the present day, commercial Chemistry and Pharmacy can best hope for success when founded on the working out of abstract scientific principles. The problem of manufacturing success is now only solved with certainty by sound and wisely-applied science.

Memorandum.—The next subject of experimental study will be determined by the nature of the student's future pursuits. In most cases the operations of quantitative analysis will engage attention. These should be of a volumetric and gravimetric character; for details concerning them see the following pages.

QUANTITATIVE ANALYSIS.

INTRODUCTORY REMARKS.

General Principles.—The proportions in which chemical substances unite with each other in forming compounds are definite and invariable (p. 47). Quantitative analysis is based on this law. When, for example, aqueous solutions of a salt of silver and a chloride are mixed, a white curdy precipitate is produced containing chlorine and silver in atomic proportions; that is, 35.4 parts of chlorine to 107.7 of silver. No matter what the chloride or what the salt of silver, the resulting chloride of silver is invariable in composition. The formula AgCl is a convenient picture of this compound in these proportions. The weight of a definite compound being given, therefore, the proportional amounts of its constituents can be ascertained by simple calculation. Suppose, for instance, 8.53 parts of chloride of silver have been obtained in some analytical operation; this amount will contain 2.11 parts of chlorine and 6.42 of silver; for if 143.1 (the molecular weight) of chloride of silver contain 35.4 (the atomic weight) of chlorine, 8.53 of chloride of silver will be found to contain 2.11 of chlorine:—

$$143.1 \;:\; 35.4 \;::\; 8.53 \;:\; x.$$

$$\begin{array}{r}
\underline{8.53} \\
1.062 \\
17.70 \\
\underline{283.2} \\
143.1)301.962(2.11 \\
\underline{286.2} \\
15.76 \\
\underline{14.31} \\
1.452 \\
\underline{1.431} \\
21
\end{array} \qquad x = 2.11.$$

And if 143.1 of chloride of silver contain 107.7 of silver, 8.53 of chloride of silver will contain very nearly 6.42 of silver. To ascertain, for example, the amount of silver in a substance containing, say, nitrate of silver, all that is necessary is to take a weighed quantity of the substance, dissolve it, precipitate the whole of the silver by adding hydrochloric acid or other chloride till no more chloride of silver falls, collect the precipitate on a filter, wash, dry, and weigh. The amount of silver in the dried chloride, ascertained by calculation, is the amount of silver in the quantity of substance on which the operation was conducted; a rule-of-three sum gives the quantity per cent., the form in which the results of quantitative analysis are usually stated. Occasionally a constituent of a substance admits of being isolated and weighed in the uncombined state. Thus the amount of mercury in a substance may be determined by separating and weighing the mercury in a metallic condition; if occurring as calomel (HgCl) or corrosive sublimate ($HgCl_2$), the proportion of chlorine may then be ascertained by calculation (Hg = 199.7; Cl = 35.4).

Nature of Gravimetric Quantitative Analysis.—As above stated, a body may be isolated and *weighed*, and its quantity thus ascertained, or it may be separated and weighed in combination with another body whose combining proportion is well known; this is quantitative analysis by the *gravimetric* method.

Nature of Volumetric Quantitative Analysis.—Volumetric operations depend for success on some accurate initial gravimetric operation. A *weighed* amount of a pure salt is dissolved in a given *volume* of water or other fluid, and thus forms *a standard solution.* Accurately *measured* quantities of such a solution will obviously contain just as definite amounts of the dissolved salt as if those amounts were actually *weighed* in a balance, and, as measuring occupies less time than weighing, the volumetric operations can be conducted with great economy of time as compared with the corresponding gravimetric operations. Quantitative analysis by the *volumetric* method consists in noting the volume of the standard liquid required to be added to the substance under examination before a given effect is produced. Thus, for instance, a solution of nitrate of silver of known strength may be used in experimentally ascertaining an unknown amount of chlorine in any substance. The silver solution is added to a solution of a definite quantity of the substance until flocks of chloride of silver cease to be precipitated: every 107.7 parts of silver added (or 169.7 of nitrate of silver: $Ag = 107.7$, $N = 14$, $O_3 = 48$; total 169.7) indicates the presence of 35.4 of chlorine or an equivalent quantity of any chloride. The preparation of standard solutions, such as that of nitrate of silver, to which allusion is here made, requires considerable care, but when made certain analyses can, as already indicated, be executed with far more rapidity and ease than by gravimetric processes.

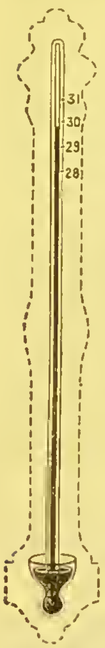
Quantitative Determination of (*a*) *Atmospheric Pressure,* (*b*) *Temperature, and* (*c*) *Weight.*—The quantitative analysis of solids and liquids often involves quantitative determinations of atmospheric pressure, temperature, and weight. These processes will now be explained, after which an outline of volumetric and gravimetric quantitative analysis will be given. The scope of this work precludes any attempt to describe all the little mechanical details observed by quantitative analysts; essential operations, however, are so fully treated that expert manipulators will meet with little difficulty.

Quantitative Determination of Atmospheric Pressure.

The Barometer.—The analysis of gases and vapors involves determinations of the varying pressure of the atmosphere as indicated by the *barometer* (from *βάρος*, *baros*, weight, and *μέτρον*, *metron*, measure).

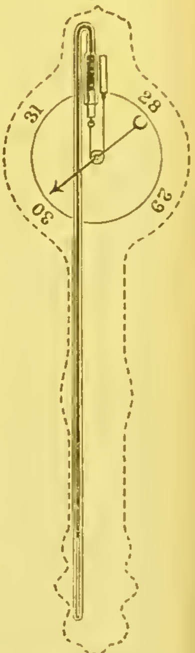
The ordinary mercurial barometer is a glass tube 33 or 34 inches long, closed at one end, filled with mercury, and inverted in a small cistern or cup of mercury (fig. 62). The mercury remains in the tube, owing to the weight or pressure of the atmosphere on the exposed surface of the liquid, the average height of the column being nearly 30 inches. In the popular form of the instrument, the wheel-barometer, the cistern is formed by a recurvature of the tube (fig. 63); on the exposed surface of the mercury a float is placed, from which a thread passes over a pulley and moves an index whenever the column of mercury rises or falls. As supplied to the public, these barometers are usually enclosed in ornamental frames with thermometers attached. In the wheel-barometer the glass tube and contained column of mercury are altogether enclosed, the index alone being visible. In the other variety the upper end of the glass tube and mercurial column are exposed, and the height of the mercury is ascertained by direct observation.

Fig. 62.



Barometer.

Fig. 63.



Barometer.

The aneroid barometer (from ἀ, *a*, *without*, and νηρὸς, *neros*, fluid) consists of a small, shallow, vacuous metal drum, the sides of which approach each other when an increase of atmospheric pressure occurs, their elasticity enabling them to recede toward their former position on a decrease of pressure. This motion is so multiplied and altered in direction by levers, etc. as to act on a hand traversing a plate on which are marked numbers corresponding with those showing the height of the mercurial column of the ordinary barometer by which the aneroid was adjusted. *The Bourdon barometer* (from the name of the inventor) is a modified aneroid, containing, in the place of the round metal box, a flattened vacuous tube of metal bent nearly to a circle. These baromters are also useful for measuring the pressure in steam-boilers, etc. Under the name of *pressure-gauges* they are sold to indicate pressure of 500 pounds and upward per square inch. From their portability (they can be made of 1 to 2 inches in diameter and 1 inch thick) they are excellent companions for travellers wishing to know the height of hills, mountains, and other elevations.

For further information concerning the influence of pressure on the volume of a gas or vapor see page 547 ; and for descriptions of the methods of analyzing gases refer to Ganot's *Physics* (translated by Atkinson), Miller's *Chemical Physics*, and "Analysis of Gases" in Watt's *Dictionary of Chemistry*.

Quantitative Determination of Temperature.

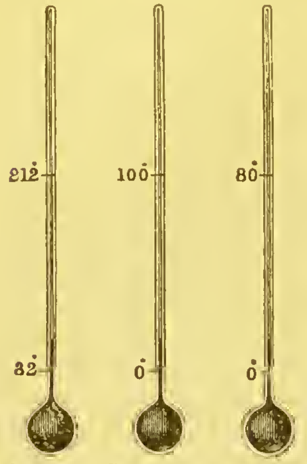
General Principles.—As a rule, all bodies expand on the addition and contract on the abstraction of heat, the alteration in volume being constant and regular for equal increments or decrements of temperature. The extent of this alteration in a given substance, expressed in parts or degrees, constitutes the usual method of intelligibly stating, with accuracy, precision, and minuteness, a particular condition of warmth or temperature—that is, of sensible heat. The substance commonly employed for this purpose is mercury, the chief advantages of which are that it will bear a high temperature without boiling, a low temperature without freezing, does not adhere to glass to a sufficient extent to "wet" the sides of any tube in which it may be enclosed, and, from its good conducting-power for heat, responds rapidly to changes of temperature. Platinum, earthenware, alcohol, and air are also occasionally used for thermometric purposes.

The Thermometer.—The construction of an accurate thermometer is a matter of great difficulty, but the following are the leading steps in the operation :—Select a piece of glass tubing having a fine capillary (*capillus*, a hair) bore and about a foot long ; heat one extremity in the blowpipe-flame until the orifice closes and the glass is sufficiently soft to admit of a bulb being blown ; heat the bulb to expel air, immediately plunging the open extremity of the tube into mercury ; the bulb having cooled, and some mercury having entered and taken the place of expelled air, again heat the bulb and tube until the mercury boils and its vapor escapes through the bore of the tube : again plunge the extremity under mercury, which will probably now completely fill the bulb and tube. When cold the bulb is placed in melting ice. The top of the column of mercury in the capillary tube should then be within an inch or two of the bulb ; if higher, some of the mercury must be expelled by heat ; if lower, more metal must be introduced as before. The tube is now heated near the open end and a portion drawn out until the diameter is reduced to about one-tenth. The bulb is next warmed until the mercurial column rises above the constricted part of the tube, which is then rapidly fused in the blowpipe-flame and the extremity of the tube removed.

The instrument is now ready for *graduation.* The bulb is placed in boiling water (a medium having, *cæteris paribus*, an invariable temperature), and when the position of the top of the mercurial column is constant a mark is made on the tube by a scratching diamond or a file. This operation is repeated with melting ice (also a medium having an invariable temperature). The space between these two marks is divided into a certain number of intervals termed *degrees.* Unfortunately, this number is not uniform in all countries : in England it is 180, as proposed by Fahrenheit ; in France 100, as proposed by Celsius (the Centigrade scale), a number generally adopted by scientific men ; in some parts of the Continent the divisions are 80 for the same interval, as suggested by Reaumur. Whichever be the number selected, similar markings should be continued beyond the boiling- and freezing-points as far as the length of the stem admits. They may be made on the stem itself or on any wood, metal, or earthenware frame on which the stem is mounted.

Fig. 64,

Thermometric Scales.



Fahrenheit. Centigrade. Reaumur.

Thermometric Scales (fig. 64).—On the Centigrade (C.) and Reaumur (R.) scales the freezing-point of water is made zero, and the boiling-point 100 and 80 respectively; on the Fahrenheit (F.) scale the zero is placed 32 degrees below the congealing-point of water, the boiling-point of which becomes, consequently, 212. Even on the Fahrenheit system, temperatures below the freezing-point of water are often spoken of as "degrees of frost;" thus 19 degrees as marked on the thermometer would be regarded as "13 degrees of frost." It is to be regretted that the freezing-point of water is not universally regarded as the zero-point, and that the number of intervals between that and the boiling-point is not everywhere the same.

The degrees of one scale are easily converted into those of another if their relations be remembered—namely: 180 (F.), 100 (C.), 80 (R.); or 18, 10, and 8; or, best, 9, 5, and 4.

Formulæ for the Conversion of Degrees of one Thermometric Scale into those of another.

F = Fahrenheit.
R = Reaumur.
C = Centigrade.
D = The observed degree.

If above the freezing-point of water (32° F; 0° C; 0° R),
F into C . . . . $(D - 32) \div 9 \times 5$.
F " R . . . . $(D - 32) \div 9 \times 4$.
C " F . . . . $D \div 5 \times 9 + 32$.
R " F . . . . $D \div 4 \times 9 + 32$.

If below freezing, but above 0° F (— 17°.77 C; — 14°.22 R),
F into C . . . . $-(32 - D) \div 9 \times 5$.
F " R . . . . $-(32 - D) \div 9 \times 4$.
C " F . . . . $32 - (D \div 5 \times 9$.
R " F . . . . $32 - (D \div 4 \times 9$.

If below 0° F (— 17°.77 C; — 14°.22 R),
F into C . . . . $-(D + 32) \div 9 \times 5$.
F " R . . . . $-(D + 32) \div 9 \times 4$.
C " F . . . . $-(D \div 5 \times 9) - 32$.
R " F . . . . $-(D \div 4 \times 9) - 32$.

For all degrees:

C into R . . . . D ÷ 5 × 4.
R " C . . . . D ÷ 4 × 5.

In ascertaining the temperature of a liquid the bulb of a thermometer is simply inserted and the degree noted. In determining the boiling-point also the bulb is inserted in the liquid, if a pure substance. In taking the boiling-point of a liquid which is being distilled from a mixture, the bulb of the thermometer should be near to but not beneath the surface.

The "boiling-point" of a liquid is the temperature at which the elasticity of the vapor of the substance overcomes the atmospheric or other pressure to which the liquid is exposed. If the pressure is equal to 760 mm. (29.92 inches) of mercury, water will boil at 100° C. (212° F.). The boiling-point of a drop of a fluid is taken by introducing it into the closed extremity of a small U-tube, the remaining portion of the closed limb being filled with mercury. The tube is lowered into a bath, the open limb being above the surface of the fluid of the bath. The bath is slowly and equally heated, and the boiling-point of the liquid, indicated by the mercury falling until it is level in the two limbs, taken by a thermometer whose bulb is close to the U-tube.

The following are the boiling-points of a few substances met with in pharmacy :—

	Centigrade.	Fahrenheit.
Alcohol, absolute	78.3	173
" 84 per cent.	79.5	175
" 49 per cent. (proof spirit) . . .	81.4	178.5
" amylic	132.2	270
Benzol	80.6	177
Bromine	63.0	145.4
Benzoic acid	239.0	462
Carbolic acid	187.8	370
Chloroform	61	142
Ether (B. P.) . . . . (below)	40.5	105
" pure	35	95
Mercury *in vacuo* (as in a thermometer) .	304	580
" in air (barom. at 30 inches) . . .	350	662
Water (barom. at 29.92 inches)	100	212
" (" 29.33 ")	99.5	211
" (" 28.74 ")	99	210
Saturated solutions of—		
Cream of tartar	101	214
Common salt	106.6	224
Sal ammoniac	113.3	236
Nitrate of sodium	119	246
Acetate of sodium	124.4	256
Chloride of calcium	179.4	355

By "gentle heat," U. S. P., is meant any temperature between about 32° C. and 38° C. (about 90° and 100° F.).

To Determine Melting-points of Fat,—Heat a fragment of the substance (spermaceti or wax, for example) till it liquefies, and then draw up a small portion into a thin glass tube about the size of a knitting-needle. Immerse the tube in cold water contained in a beaker, and slowly heat the vessel till the thin opaque cylinder of solid fat melts and becomes transparent; a delicate thermometer placed in the water indicates the point of change to the fifth of a degree. Remove the source of heat and note the congealing-point of the substance; it will be identical with or close to the melting-point.

Pyrometers.—Temperatures above the boiling-point of mercury are determined by ascertaining to what extent a bar of platinum or porcelain has elongated. The bar is enclosed in a cavity of a suitable case, a plug of platinum or porcelain placed at one end of the bar, and the whole exposed in the region the temperature of which is to be found. After cooling, the distance to which the bar has forced the plug along the cavity is accurately measured and the corresponding degree of temperature noted. The value of the distance is fixed for low temperatures by comparison with a mercurial thermometer, and the scale carried upward through intervals of equivalent length. Such thermometers are conventionally distinguished from ordinary instruments by the name *pyrometer* (from πυρ, *pur*, fire, and μέτρον, *metron*, measure).

The following are melting-points of substances official in the British Pharmacopœia:—

	In degrees Centigrade.	In degrees Fahrenheit.
Acetic acid, glacial	8.9	48
" " " congeals at	1.1	34
Benzoic acid	120	248
Carbolic acid	35	95
Oil of theobroma (about)	32	90
Phosphorus	43.3	110
Prepared lard (about)	38	100
" suet	39.5	103
Spermaceti (not under)	38	100
White wax	65.5	150
Yellow wax	60	140

The order of fusibility of a few of the metals is as follows:—

	In degrees Centigrade.	In degrees Fahrenheit.
Mercury	— 39.4	— 39
Potassium	+ 62.5	+ 144.5
Sodium	97.6	207.7
Tin	227.8	442
Bismuth	264	507
Lead	325	617
Zinc	411.6	773
Antimony	621	1150
Silver	1023	1873
Copper	1091	1996
Gold	1102	2016
Cast iron	1530	2786

QUESTIONS AND EXERCISES.

922. On what fundamental laws are the operations of quantitative analysis based?

923. What is the general nature of *gravimetric* quantitative analysis?

924. Describe the general principle of *volumetric* quantitative analysis.

925. How are variations in atmospheric pressure quantitatively determined?

926. Explain the construction and mode of action of a mercurial barometer.

927. In what respect does a wheel-barometer differ from an instrument in which the readings are taken from the top of the column of mercury?

928. Describe the principle of action of an aneroid barometer.

929. On what general principles are thermometers constructed?

930. What material is employed in making thermometers?

931. Why is mercury selected as a thermometric indicator?

932. Describe the manufacture of a mercurial thermometer.

933. How are thermometers graduated?

934. Give formulæ for the conversion of the degrees of one thermometric scale into those of another, (*a*) when the temperature is above the freezing-point of water, (*b*) below 32° F., but above 0° F., and (*c*) below 0°.

935. Name the degree C. equivalent to 60° F.

936. What degree C. is represented by — 4° F.?

937. Mention the degree F. indicated by 23° C.

938. Convert 100° R. into degrees C. and F.

939. State the boiling-points of alcohol, chloroform, ether, mercury, and water on either thermometric scale.

940. Describe the details of manipulation in estimating the melting-point of fats.

941. In what respect do pyrometers differ from thermometers?

942. Mention the melting-points of glacial acetic acid, oil of theobroma, lard, suet, and wax.

943. Give the fusing-points of tin, lead, zinc, copper, and cast-iron.

Quantitative Determination of Weight.

Definitions.

All bodies, celestial and terrestrial, attract each other, the amount of attraction being in direct proportion to the quantity of matter of which they consist, and in inverse proportion to the squares of their distances. This is *gravitation.* When gravitation in certain directions is exactly counterbalanced by gravitation in opposite directions, a body (*e. g.* the earth) remains suspended in space. Such a body in relation to other bodies has gravity, but not weight. *Weight* is the effect of gravity, being the excess of gravitation in one direction over and above that exerted in the opposite direction. Weight, truly, in any terrestrial substance is the excess of attraction which it and the earth have for each other over and above the attraction of each in opposite directions by the various heavenly bodies. But, practically, the weight of any terrestrial substance is the effect of the attraction of the earth only. *Specific* weight is the definite or precise weight of a body in relation to its bulk; it is more usually but not quite correctly termed *specific gravity*—gravity belonging to the earth, and not, in any sensible degree, to the substance.

QUESTIONS.

944. What is understood by gravitation?

945. State the difference between weight and gravity.

946. Mention a case in which a body has gravity, but no apparent weight.

947. Practically, what causes the weight of terrestrial substances?

Weights and Measures.

The Balance.—The balance used in the quantitative operations of analytical chemistry must be accurate and sensitive. The points of suspension of the beam and pans should be polished steel or agate knife-edges working on agate planes. It should turn easily and quickly, without too much oscillation, to $\frac{1}{500}$ or $\frac{1}{600}$ of a grain or $\frac{1}{10}$ of a milligramme, when 1000 grains or 50 or 60 grammes are placed in each scale. (Grammes are weights of the metric system, a description of which is given on the next two or three pages.) The beam should be light and strong, capable of supporting a load of 1500 grains or 100 grammes; its oscillations are observed by help of a long index attached to its centre, and continued downward for some distance in front of the supporting pillar of the balance. The instrument should be provided with screws for purposes of adjustment, a mechanical contrivance for supporting the beam above its bearing when not in use or during the removal or addition of weights, spirit-levels to enable the operator to give it a horizontal position, and be enclosed in a glass case to protect from dust. It should be placed in a room the atmosphere of which is not liable to be contaminated by acid fumes, in a situation free from vibration, and a vessel containing lumps of quicklime should be placed in the case to keep the enclosed air dry and prevent the formation of rust on any steel knife-edges or other parts. During weighing the doors of the balance should be shut, in order that currents of air may not unequally influence the pans.

The Weights.—These should be preserved in a box having a separate compartment for each. They must not be lifted directly with the fingers, but by a small pair of forceps. If grain-weights, they should range from 1000 grs. to $\frac{1}{10}$ gr., a $\frac{1}{10}$ weight being fashioned of gold wire to act as a "rider" on the divided beam, and thus indicate by its position 100ths and 1000ths of a grain. From $\frac{1}{10}$ to 10 grs. the weights may be of platinum; thence upward, to 1000 grs., of brass. The relation of the weights to each other should be decimal. Metric decimal weights may range from 1000 grammes to 1 gramme of brass, and thence downward to 1 centigramme of platinum, a gold centigramme rider being employed to indicate milligrammes and tenths of a milligramme.

Weights and Measures of the U. S. Pharmacopœia.—"The working formulæ of the United States Pharmacopœia are now so constructed that, in their practical application, any system of weights or (in certain cases measures) may be used." "The weights and measures referred to by physicians in prescribing, and used by pharmacists in dispensing medicines, are, in the United States, either those of the 'apothecaries' or troy system of weights and the wine measure, or those of the metric system."

Troy Weights.—These are derived from the *troy pound*, and are exhibited in the following table, with their signs annexed:—

One pound,	℔	= 12 ounces	= 5760 grains.
One ounce,	℥	= 8 drachms	= 480 grains.
One drachm,	ʒ	= 3 scruples	= 60 grains.
One scruple,	℈	. . . . . .	= 20 grains.
One grain,	gr.	. . . . . .	= 1 grain.

It is highly important that persons engaged in preparing medicines should be provided with troy weights. But those who are not so provided can make their avoirdupois weights available as substitute for troy weights by bearing in mind that 42.5 grains, added to the avoirdupois ounce, will make it equal to the troy ounce, and that 1240 grains, deducted from the avoirdupois pound, will reduce it to the troy pound.

Measures.—These are derived from the *wine gallon*, and are given in the following table, with their signs annexed:—

One gallon,	C	= 8 pints	= 61,440 minims.
One pint,	O	= 16 fluidounces	= 7,680 minims.
One fluidounce,	f℥	= 8 fluidrachms	= 480 minims.
One fluidrachm,	fʒ	. . . .	= 60 minims.
One minim,	♏	. . . .	= 1 minim.

Relation of Troy Weight and Wine Measure.

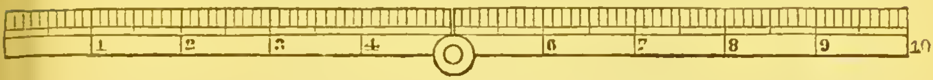
1 minim =	0.95 grains.	1 grain =	1.05 minims.
1 fʒ =	56.96 "	1 ʒ =	63.2 "
1 f℥ =	455.69 "	1 ℥ =	505.6 "

The Metric System of weights (the word *metric* is from the Greek *μέτρον*, *metron*, measure) is greatly to be preferred to all others, the relation of the metric weights of all denominations to measures of length, capacity, and surface being so simple as to be within the perfect comprehension of a child; while under the British and American plans the weights have no such relation either with each other or with the various measures. Moreover, the metric system is in perfect harmony with the universal method of counting; it is a decimal system.

[It is perhaps impossible to realize, much more express, the advantages we enjoy from the fact that in every country of the world the system of numeration is identical. That system is the decimal. Whatever language a man speaks, his method of numbering is decimal; his talk concerning number is decimal; his written or printed signs signifying number are decimal. With the figures, 1, 2, 3, 4, 5, 6, 7, 8, 9, 0 he represents all possible variation in number, the position of a figure in reference to its companions alone determining its value, a figure on the left hand of any other figure in an allocation of numeral symbols (for example, 1871) having ten times the value of that figure, while the figure on the right hand of any other has a tenth of the value of that other. When the youngest pupil is asked how many units there are in 1871, he smiles at the simplicity of the question, and says 1871. How many tens? 187, and 1 over. How many hundreds? 18, and 71 over. How many thousands? 1, and 871 over. But if he is asked how many scruples there are in 1871 grains, how many drachms, how many ounces, he first inquires which drachms or which ounces are meant—avoirdupois ounces, troy ounces, or wine ounces—and then brings out his slate and pencil. And so with the pints or gallons in 1871 fluidounces, or the feet and yards in 1871 inches, or the pence, shillings, and pounds in 1871 farthings; to say nothing of cross questions, such as the value of 1871 articles at 2 dollars and 20 cents per dozen, or of the perplexity caused by the varying values of several individual weights or of measures of length, capacity, and surface in different parts of the country. What is desired is, that there should be an equally simple decimal relation among weights and measures and coins as already universally exists among numbers. This condition of things having already been introduced into most other countries, there is no good reason why it should not be accomplished in the United States and Great Britain.]

The Metric System of weights and measures is founded on the metre. The engraving (Fig. 65) represents a pocket folding-measure, the tenth part of a metre in length, divided into ten centimetres, and each centimetre into 10 millimetres.

Fig. 65.



The Decimetre.

The units of the system with their multiples and submultiples are as follows:—

UNITS.

Length.—The *Unit of Length* is the METRE, derived from the measurement of the quadrant of a meridian of the earth. (Practically, it is the length of certain carefully-preserved bars of metal from which copies have been taken.)

Surface.—The *Unity of Surface* is the ARE, which is the square of ten metres.

Capacity.—The *Unity of Capacity* is the LITRE, which is the cube of a tenth part of a metre.

Weight.—The *Unit of Weight* is the GRAMME, which is the weight of that quantity of distilled water, at its maximum density (4° C.), which fills a cube of the one-hundredth part of the metre.

TABLE.

Note.—Multiples are denoted by the Greek words "Deca," Ten, "Hecto," Hundred, "Kilo," Thousand.

Subdivisions, by the Latin words "Deci," One-tenth, "Centi," One-hundredth, "Milli," One-thousandth.

Quantities.	Length.	Surface.	Capacity.	Weight.
1000	Kilo-metre	. . .	Kilo-litre	Kilo-gramme.
100	Hecto-metre	Hectare	Hecto-litre	Hecto-gramme.
10	Deca-metre	. . .	Deca-litre	Deca-gramme.
1 (Units)	**METRE**	**ARE**	**LITRE**	**GRAMME.**
.1	Deci-metre	. . .	Deci-litre	Deci-gramme.
.01	Centi-metre	Centiare	Centi-litre	Centi-gramme.
.001	Milli-metre	. . .	Milli-litre	Milli-gramme.

When the Metric Method is exclusively adopted these units and this table, comprising the entire system of weights and measures, represent all that will be essential to be learned in lieu of the numerous and complicated tables hitherto in use. Adopting the style of elementary books on arithmetic, the Tables may be expanded in the following manner:—

10 Milligrammes make 1 Centigramme.
10 Centigrammes " 1 Decigramme.
10 Decigrammes " 1 Gramme.
10 Grammes " 1 Decagramme.
10 Decagrammes " 1 Hectogramme.
10 Hectogrammes " 1 Kilogramme.

10 Millilitres make 1 Centilitre,
etc.

10 Millimetres make 1 Centimetre,
etc.

The following approximate equivalents of metrical units should be committed to memory:—

1 Metre = 3 feet 3 inches and 3 eighths.
1 Are = a square whose side is 11 yards.
1 Litre = 1¾ pints.
1 Gramme = 15½ grains.

The Kilometre is equal to 1100 yards.
The Hectare = 2½ acres nearly.
The Metric Ton of 1000 Kilogrammes = 19 cwt. 2 qrs. 20 lbs. 10 oz.
The Kilogramme = 2 lbs. 3¼ oz. nearly.

For *exact* equivalents in many forms see pages 539 and 540. A litre of water at 39° F. weighs 15432 grains; at 50° F., 15429 grains; at 60° F., it weighs 15418 grains; at 70° F., 15403 grains; and at 80° F., 15383 grains (Pile). (The word *gramme* is, in English, frequently written *gram.*)

Decimal Coinage.—In most countries where the metric system of weights and measures is employed a decimal division of coins is also adopted. This course, conjoined with the ordinary decimal method of enumerating, which, fortunately, is in universal use, renders calculations of all kinds most simple—easy to an extent which cannot be conceived in countries like England, where the operations of weighing, measuring, paying, and counting have only the most absurdly intricate relations to each other.

The General Council under whose authority the British Pharmacopœia is issued encourages medical practitioners and pharmacists in the adoption of the metric system, and gives the annexed statement of metric weights and measures:—

WEIGHTS AND MEASURES OF THE METRICAL SYSTEM.

(From the British Pharmacopœia of 1867.)

WEIGHTS.

1 Milligramme	= the thousandth part of one grm., or	0.001	grm.
1 Centigramme	= the hundredth "	0.01	"
1 Decigramme	= the tenth "	0.1	"
1 Gramme	= weight of a cubic centimetre of water at 4° C.	1.0	"
1 Decagramme	= ten grammes	10.0	"
1 Hectogramme	= one hundred grammes	100.0	"
1 Kilogramme	= one thousand grammes	1000.0	(1 kilo.).

MEASURES OF CAPACITY.

1 Millilitre	=	1	cub. centim.,	or the meas. of	1	gram.	of water.
1 Centilitre	=	10	"	"	10	"	"
1 Decilitre	=	100	"	"	100	"	"
1 Litre	=	1000	"	"	1000	"	(1 kilo.).

MEASURES OF LENGTH.

1 Millimetre	= the thousandth part of one metre, or	0.001	metre.
1 Centimetre	= the hundredth "	0.01	"
1 Decimetre	= the tenth "	0.1	"
1 Metre	= the ten-millionth part of a quarter of the meridian of the earth.		

The National Convention for revising the Pharmacopœia of the United States also recognizes the metric system of weights and measures by giving, in the recent (sixth) edition of the Pharmacopœia, Tables of the units of the metrical system with their multiples and submultiples, similar to the foregoing, and the following Tables showing the relation to each other of the metrical and troy systems. In some parts of the text of the work the metric system is that actually employed.

TABLES OF WEIGHTS AND MEASURES.

A.—MEASURES OF LENGTH.

I. RELATION OF METRIC TO UNITED STATES MEASURES OF LENGTH.

1 Metre	=	39.370432	inches.
1 Decimetre	=	3.937043	"
1 Centimetre	=	0.393704	"
1 Millimetre	=	0.039370	"

II. RELATION OF UNITED STATES TO METRIC MEASURES OF LENGTH.

1 Yard (or 36 Inches) = 0.91439 Metre.
1 Foot (or 12 Inches) = 30.40 Centimetres.

Inches.		Centimetres.	Inches.		Centimetres.	Inch.		Centimetres
11	=	27.9	5	=	12.7	$\frac{1}{2}$	=	12.5
10	=	25.4	4	=	10.2	$\frac{1}{4}$	=	6.25
9	=	22.9	3	=	7.6	$\frac{1}{8}$	=	3.12
8	=	20.3	2	=	5.1	$\frac{1}{16}$	=	1.54
7	=	17.8	1	=	2.5	$\frac{1}{25}$	=	1.00
6	=	15.2						

B.—MEASURES OF CAPACITY.

III. RELATION OF METRIC TO UNITED STATES FLUID MEASURES.

Cubic Centim.		Fluidounces.	Cubic Centim.		Fluidrachms.	Cubic Centim.		Minims
1,000	=	33.81	15	=	4.06	0.40	=	6.49
950	=	32.12	10	=	2.71	0.35	=	5.68
900	=	30.43	9	=	2.43	0.30	=	4.87
850	=	28.74	8	=	2.16	0.25	=	4.06
800	=	27.05	7	=	1.89	0.20	=	3.25
750	=	25.36	6	=	1.62	0.19	=	3.08
700	=	23.67	5	=	1.35	0.18	=	2.92
650	=	21.98	4	=	1.08	0.17	=	2.76
600	=	20.29				0.16	=	2.60
550	=	18.59	Cubic Centim.		Minims.	0.15	=	2.43
500	=	16.90	3	=	48.69	0.14	=	2.27
450	=	15.22	2	=	32.46	0.13	=	2.11
400	=	13.53	1	=	16.23	0.12	=	1.95
350	=	11.84	0.95	=	15.42	0.11	=	1.79
300	=	10.14	0.90	=	14.61	0.10	=	1.62
250	=	8.45	0.85	=	13.80	0.09	=	1.46
200	=	6.76	0.80	=	12.98	0.08	=	1.30
150	=	5.07	0.75	=	12.17	0.07	=	1.14
100	=	3.38	0.70	=	11.36	0.06	=	0.97
30	=	1.01	0.65	=	10.55	0.05	=	0.81
			0.60	=	9.74	0.04	=	0.65
Cubic Centim.		Fluidrachms.	0.55	=	8.93	0.03	=	0.49
25	=	6.76	0.50	=	8.12	0.02	=	0.32
20	=	5.41	0.45	=	7.30	0.01	=	0.16

IV. RELATION OF UNITED STATES TO METRIC FLUID MEASURES.

Minims.		Cubic Centim.	Minims.		Cubic Centim.	Minims.		Cubic Centim
1	=	0.06	8	=	0.49	15	=	0.92
2	=	0.12	9	=	0.55	16	=	0.99
3	=	0.18	10	=	0.62	17	=	1.05
4	=	0.25	11	=	0.68	18	=	1.11
5	=	0.31	12	=	0.74	19	=	1.17
6	=	0.37	13	=	0.80	20	=	1.23
7	=	0.43	14	=	0.86	21	=	1.29

RELATION OF UNITED STATES TO METRIC FLUID MEASURES.—*Cont.*

Minims.		Cubic Centim.	Fluidrachms.		Cubic Centim.	Fluidounces.		Cub. Centim.
22	=	1.36	3	=	11.09	11	=	325.25
23	=	1.42	4	=	14.79	12	=	354.82
24	=	1.48	5	=	18.48	13	=	384.40
25	=	1.54	6	=	22.18	14	=	413.97
26	=	1.60	7	=	25.88	15	=	443.54
27	=	1.66	8	=	29.57	16	=	473.11
28	=	1.73	9	=	33.27	17	=	502.69
29	=	1.79	10	=	36.97	18	=	532.26
30	=	1.85	11	=	40.66	19	=	561.93
35	=	2.16	12	=	44.36	20	=	591.50
40	=	2.46	13	=	48.06	21	=	621.08
45	=	2.77	14	=	51.75	22	=	650.65
50	=	3.08	15	=	55.45	23	=	680.22
55	=	3.39	16	=	59.10	24	=	709.80
60	=	3.70				25	=	739.37
70	=	4.31	Fluidounces.			26	=	768.94
80	=	4.93	3	=	88.67	27	=	798.51
90	=	5.54	4	=	118.24	28	=	828.09
100	=	6.16	5	=	147.81	29	=	857.66
110	=	6.78	6	=	177.39	30	=	887.23
120	=	7.39	7	=	206.96	31	=	916.80
			8	=	236.53	32	=	946.38
			9	=	266.10	64	=	1892.75
			10	=	295.68	128	=	3785.51

C.—WEIGHTS.

V. RELATION OF METRIC TO APOTHECARIES' OR TROY WEIGHT.

Grammes.		Grains.	Grammes.		Grains.	Grammes.		Grains.
0.0010	=	0.015	0.0125	=	0.193	0.120	=	1.852
0.0013	=	0.019	0.0150	=	0.231	0.130	=	2.006
0.0015	=	0.023	0.0200	=	0.309	0.140	=	2.161
0.0020	=	0.031	0.0250	=	0.386	0.150	=	2.315
0.0025	=	0.039	0.0300	=	0.463	0.160	=	2.469
0.0030	=	0.046	0.0350	=	0.540	0.170	=	2.623
0.0035	=	0.054	0.0400	=	0.617	0.180	=	2.778
0.0040	=	0.062	0.0450	=	0.694	0.190	=	2.932
0.0045	=	0.069	0.050	=	0.772	0.200	=	3.086
0.0050	=	0.077	0.055	=	0.849	0.210	=	3.241
0.0055	=	0.085	0.060	=	0.926	0.220	=	3.395
0.0060	=	0.093	0.065	=	1.003	0.230	=	3.549
0.0065	=	0.100	0.070	=	1.080	0.240	=	3.704
0.0070	=	0.108	0.075	=	1.157	0.250	=	3.858
0.0075	=	0.116	0.080	=	1.235	0.260	=	4.012
0.0080	=	0.123	0.085	=	1.312	0.270	=	4.167
0.0085	=	0.131	0.090	=	1.389	0.280	=	4.321
0.0090	=	0.139	0.095	=	1.466	0.290	=	4.475
0.0095	=	0.147	0.100	=	1.543	0.300	=	4.630
0.0100	=	0.154	0.110	=	1.698	0.310	=	4,784

RELATION OF METRIC TO APOTHECARIES' OR TROY WEIGHT.—*Cont.*

Grammes.		Grains.	Grammes.		Grains.	Grammes.		Grains.
0.320	=	4.938	13	=	200.621	39	=	601.862
0.330	=	5.093	14	=	216.053	40	=	617.294
0.340	=	5.247	15	=	231.485	50	=	771.617
0.350	=	5.401	16	=	246.918	60	=	925.941
0.360	=	5.556	17	=	262.350	70	=	1080.264
0.370	=	5.710	18	=	277.782	80	=	1234.588
0.380	=	5.864	19	=	293.215	90	=	1388.911
0.390	=	6.019	20	=	308.647	100	=	1543.235
0.400	=	6.173	21	=	324.079	125	=	1929.044
0.500	=	7.716	22	=	339.512	150	=	2314.852
0.600	=	9.259	23	=	354.944	200	=	3086.470
0.700	=	10.803	24	=	370.376	250	=	3858.087
0.800	=	12.346	25	=	385.809	300	=	4629.705
0.900	=	13.889	26	=	401.241	333	=	5144.118
1	=	15.432	27	=	416.673	350	=	5401.322
2	=	30.865	28	=	432.106	400	=	6172.940
3	=	46.297	29	=	447.538	450	=	6944.557
4	=	61.729	30	=	462.970	500	=	7716.174
5	=	77.162	31	=	478.403	600	=	9259.409
6	=	92.594	32	=	493.835	700	=	10802.644
7	=	108.026	33	=	509.268	750	=	11574.262
8	=	123.459	34	=	524.700	800	=	12345.879
9	=	138.891	35	=	540.132	900	=	13889.114
10	=	154.323	36	=	555.565	1000	=	15432.350
11	=	169.756	37	=	570.997			
12	=	185.188	38	=	586.429			

VI. THE RELATION OF APOTHECARIES' (OR TROY) TO METRIC WEIGHT.

Grains.		Grammes.	Grains.		Grammes.	Grains.		Grammes.
$\frac{1}{64}$	=	0.00101	$\frac{1}{4}$	=	0.01620	14	=	0.90718
$\frac{1}{60}$	=	0.00108	$\frac{1}{3}$	=	0.02160	15	=	0.97198
$\frac{1}{50}$	=	0.00130	$\frac{1}{2}$	=	0.03240	16	=	1.037
$\frac{1}{48}$	=	0.00135	$\frac{3}{4}$	=	0.04860	17	=	1.102
$\frac{1}{40}$	=	0.00162	1	=	0.06480	18	=	1.166
$\frac{1}{36}$	=	0.00180	$1\frac{1}{2}$	=	0.09720	19	=	1.231
$\frac{1}{32}$	=	0.00202	2	=	0.12960	20	=	1.296
$\frac{1}{30}$	=	0.00216	$2\frac{1}{2}$	=	0.16200	21	=	1.361
$\frac{1}{25}$	=	0.00259	3	=	0.19440	22	=	1.426
$\frac{1}{24}$	=	0.00270	4	=	0.25920	23	=	1.458
$\frac{1}{20}$	=	0.00324	5	=	0.32399	24	=	1.555
$\frac{1}{18}$	=	0.00360	6	=	0.38879	25	=	1.620
$\frac{1}{16}$	=	0.00405	7	=	0.45359	26	=	1.685
$\frac{1}{15}$	=	0.00432	8	=	0.51839	27	=	1.749
$\frac{1}{12}$	=	0.00540	9	=	0.58319	28	=	1.814
$\frac{1}{10}$	=	0.00648	10	=	0.64799	29	=	1.869
$\frac{1}{8}$	=	0.00810	11	=	0.71297	30	=	1.944
$\frac{1}{6}$	=	0.01080	12	=	0.77759	40	=	2.592
$\frac{1}{5}$	=	0.01296	13	=	0.84239	50	=	3.240

Relation of Apothecaries' (or Troy) to Metric Weight.—*Cont.*

Drachms.		Grammes.	Ounces.		Grammes.	Ounces.		Grammes.
1	=	3.888	1½	=	46.655	11	=	342.138
2	=	7.776	2	=	62.207	12	=	373.250
3	=	11.664	3	=	93.310	13	=	404.345
4	=	15.552	4	=	124.414	14	=	435.449
5	=	19.440	5	=	155.517	15	=	466.552
6	=	23.328	6	=	186.621	16	=	497.656
7	=	27.216	7	=	217.724	17	=	528.759
			8	=	248.823	18	=	559.863
Ounces.			9	=	279.931	19	=	590.966
1	=	31.103	10	=	311.035	20	=	622.070

VII. Relation of Metric to Avoirdupois Weight.

		Avoirdupois Ounces and Grains.				Avoirdupois Ounces and Grains.				Avoirdupois Ounces and Grains.	
Grammes.		Oz.	Grs.	Grammes.		Oz.	Grs.	Grammes.		Oz.	Grs.
28.35	=	1		50	=	1	334	500	=	17	279
29	=	1	10	60	=	2	50½	550	=	19	175
30	=	1	25½	70	=	2	205	600	=	21	72
31	=	1	41	80	=	2	359	650	=	22	405½
32	=	1	56½	90	=	3	76½	700	=	24	303
33	=	1	72	100	=	3	230½	750	=	26	198½
34	=	1	87½	150	=	5	127	800	=	28	96
35	=	1	103	200	=	7	24	850	=	29	429
36	=	1	118	250	=	8	358	900	=	31	326½
37	=	1	133½	300	=	10	255	950	=	33	222
38	=	1	149	350	=	12	151½	1000	=	35	120
39	=	1	164½	400	=	14	48				
40	=	1	180	450	=	15	382				

VIII. Relation of Avoirdupois to Metric Weight.

Avoirdupois Ounces.		Grammes.	Avoirdupois Ounces.		Grammes.	Avoirdupois Pounds.		Grammes.
1/16	=	1.772	7	=	198.447	1	=	453.592
⅛	=	3.544	8	=	226.796	2	=	907.18
¼	=	7.088	9	=	255.146	3	=	1360.78
½	=	14.175	10	=	283.496	4	=	1814.37
1	=	28.350	11	=	311.846	5	=	2267.96
2	=	56.699	12	=	340.195	6	=	2721.55
3	=	85.049	13	=	368.544	7	=	3175.14
4	=	113.398	14	=	396.894	8	=	3628.74
5	=	141.748	15	=	425.243	9	=	4082.33
6	=	170.098				10	=	4535.92

The following Tables, from the British Pharmacopœia and the Diary of Messrs. De La Rue, will be found useful for reference:—

WEIGHTS AND MEASURES OF THE BRITISH PHARMACOPŒIA OF 1867.

WEIGHTS.

1 Grain	gr.	
1 Ounce	oz.	= 437.5 grains.
1 Pound	lb. = 16 ounces	= 7000 "

MEASURES OF CAPACITY.

1 Minim	min.	
1 Fluidrachm	fl. dr.	= 60 minims.
1 Fluidounce	fl. oz.	= 8 fluidrachms.
1 Pint	O.	= 20 fluidounces.
1 Gallon	C.	= 8 pints.

MEASURES OF LENGTH.

1 line = $\frac{1}{12}$ inch.

1 inch = $\frac{1}{39.1393}$ seconds-pendulum.

12 " = 1 foot.
36 " = 3 feet = 1 yard.

Length of pendulum vibrating seconds of mean time in the latitude of London in a vacuum at the level of the sea . . . . } 39.1393 inches.

(1 cubic inch of distilled water at 62° F. and 30 inches barom. = 252.458 grains.)

RELATION OF BRITISH MEASURES TO WEIGHTS.

1 Minim	is the measure of		0.91	grain of water.
1 Fluidrachm	"		54.68	grains of water.
1 Fluidounce	"	1 ounce or	437.5	"
1 Pint	"	1.25 pounds or	8750.0	"
1 Gallon	"	10 pounds or	70,000.0	"

(Gtt. = *guttæ*, drops. The term "drop" indicates a quantity which is indefinite, and should only be used when approximativeness is alone desired.)

RELATION OF WINE MEASURES TO CUBIC MEASURE.

One Gallon	=	231.	Cubic Inches.
One Pint	=	28.875	Cubic Inches.
One Fluidounce	=	1.80468	Cubic Inches.
One Fluidrachm	=	0.22558	Cubic Inch.
One Minim	=	0.00375	Cubic Inch.

METRICAL MEASURES OF LENGTH.

	In English inches.	In English feet = 12 inches.	In English yards = 3 feet.	In English fathoms = 6 feet.	In English miles = 1760 yards.
Millimetre	0.03937	0.003281	0.0010936	0.0005468	0.0000006
Centimetre	0.39371	0.032809	0.0109363	0.0054682	0.0000062
Decimetre	3.93708	0.328090	0.1093633	0.0546816	0.0000621
Metre	**39.37079**	3.280899	1.0936331	0.5468165	0.0006214
Decametre	393.70790	32.808992	10.9363310	5.4681655	0.0062138
Hectometre	3937.07900	328.089920	109.3633100	54.6816550	0.0621382
Kilometre	39370.79000	3280.899200	1093.6331000	546.8165500	0.6213824
Myriometre	393707.90000	32808.992000	10936.3310000	5468.1655000	6.2138244

1 inch = 2.539954 centimetres.

1 foot = 3.0479449 decimetres.

1 yard = 0.9143835 metre.

1 mile = 1.6093149 kilometres.

METRICAL MEASURES OF SURFACE.

	In English square feet.	In Eng. sq. yards = 9 square feet.	In English poles = 272.25 sq. feet.	In English roods = 10890 sq. feet.	In English acres = 43560 sq. feet.
Centiare, or square metre	10.764299	1.196033	0.0395383	0,0009885	0.0002471
Are, or 100 square metres	1076.429934	119.603326	3.9538290	0.0988457	0.0247114
Hectare, or 10,000 square metres	107642.993418	11960.332602	395.3828959	9.8845724	2.4711431

1 square inch = 6.4513669 square centimetres.

1 square foot = 9.2899683 square decimetres.

1 square yard = 0.83609715 square metre or centiare.

1 acre = 0.40467102 hectare.

METRICAL MEASURES OF CAPACITY.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34.65923 cubic inches.	In gallons = 8 pints = 277.27384 cubic inches.	In bushels = 8 gallons = 2218.19072 cubic inches.
Millilitre, or cubic centimetre.......	0.06103	0.000035	0.00176	0.0002201	0.0000275
Centilitre, or 10 cubic centimetres..	0.61027	0.000353	0.01761	0.0022010	0.0002751
Decilitre, or 100 cubic centimetres..	6.10271	0.003532	0.17608	0.0220097	0.0027512
Litre, or cubic decimetre.............	61.02705	0.035317	**1.76077**	0.2200967	0.0275121
Decalitre, or centistere.................	610.27052	0.353166	17.60773	2.2009668	0.2751208
Hectolitre, or decistere.................	6102.70515	3.531658	176.07734	22.0096677	2.7512085
Kilolitre, or stere, or cubic metre...	61027.05152	35.316581	1760.77341	220.0966767	27.5120846
Myriolitre, or decastere................	610270.51519	353.165807	17607.73414	2200.9667675	275.1208459

1 cubic inch = 16.386176 cubic centimetres. 1 cubic foot = 28.315312 cubic decimetres. 1 gallon = 4.535926 litres.

METRICAL MEASURES OF WEIGHT.

	In English grains.	In troy ounces = 480 grains.	In avoirdupois lbs. = 7000 grains.	In cwts. = 112 lbs. = 784000 grains.	Tons = 20 cwts. = 15680000 grains.
Milligramme	0.01543	0.000032	0.0000022	0.0000000	0.0000000
Centigramme	0.15432	0.000322	0.0000220	0.0000002	0.0000000
Decigramme................................	1.54323	0.003215	0.0002205	0.0000020	0.0000001
Gramme.....................................	**15.43235**	0.032151	0.0022046	0.0000197	0.0000010
Decagramme	154.32349	0.321507	0.0220462	0.0001968	0.0000098
Hectogramme..............................	1543.23488	3.215073	0.2204621	0.0019684	0.0000984
Kilogramme	15432.34880	32.150727	2.2046213	0.0196841	0.0009842
Myriogramme..............................	154323.48800	321.507267	22.0462126	0.1968412	0.0098421

1 grain = 0.064799 gramme. 1 troy oz. = 31.103496 grammes. 1 lb. avd. = 0.453593 kilogr. 1 cwt. = 50.802377 kilogrs.

QUESTIONS AND EXERCISES.

948. Mention some advantages of a decimal system of weights and measures.

949. What is the name of the chief unit of the metric decimal system of weights and measures?

950. Mention the names of the metric units of surface, capacity, and weight, and state how they are derived from the unit of length.

951. How are multiples of metric units indicated?

952. State the designations of submultiples of metric units.

953. How many metres are there in a kilometre?

954. How many millimetres in a metre?

955. How many grammes in 5 kilogrammes?

956. How many milligrammes in 13½ grammes?

957. In 1869 centigrammes how many grammes?

958. In a metre measure 5 centimetres wide and 1 centimetre thick, how many cubic centimetres?

959. How many litres are contained in a cubic metre of any liquid?

960. State the British equivalent of the metre.

961. How many square yards in an are?

962. How many fluidounces in a litre?

963. How many ounces in a kilogramme?

964. Give the relation of a metric ton (1000 kilos.) to a British ton.

965. How many grains are there in 1 ton?

966. How many ounces in 1 ton?

967. How many grains of water in 1 fluidrachm?

968. How many minims in 1 pint?

969. How many grains in 1 pint of water?

970. Whence is the British unit of length derived?

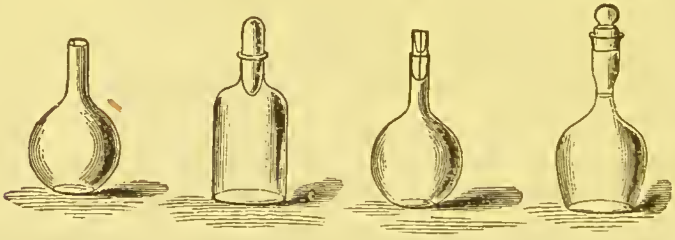
Specific Weight or Specific Gravity.

The *specific weight* of a substance is its weight in comparison with weights of similar bulks of other substances. This comparative heaviness of *solids and liquids* is conventionally expressed in relation to water: they are considered as being lighter or heavier than water. Thus, water being regarded as unity = 1, the relative weight, or specific weight, of ether is represented by the figures .720 (it is nearly three-fourths, .750, the weight of water), oil of vitriol by 1.843 (it is nearly twice, 2.000, as heavy as water). The specific weight of substances is, moreover, by generally accepted agreement, the weight of similar volumes at 15° C. (59° F.), except in the case of alcohol and wine, which are at present taken at 15.6° C. (60° F.), to maintain consistency with United States laws and regulations; for the weight of a definite volume of any substance will vary according to temperature, becoming heavier when cooled and lighter when heated, different bodies (gases excepted) differing in their rate of contraction and expansion. While, then, specific weight—or, conventionally, *specific gravity*—is truly the comparative weight of equal bulks, the numbers which in America commonly represent specific gravities are the comparative weights of equal bulks at 15° C. (59° F.), water being taken as unity.* The standard of comparison for gases was formerly air, but is now usually hydrogen.

SPECIFIC GRAVITY OF LIQUIDS..

Procure any small bottle holding from 100 to 1000 grains (fig. 66) and having a narrow neck; counterpoise it in a delicate balance; fill it to about halfway up the neck with pure distilled water having a temperature of 15° C.; ascertain the weight of the water, and, for convenience, add or subtract a drop or two, so that the weight shall be a round number of grains; mark the neck by a diamond or file-point at the part cut by the lower edge of the curved surface of the water. Consecutively fill up the bottle to the neck-mark with several other liquids, cooled or warmed to 15° C., first rinsing out the bottle once or twice with a small quantity of each liquid, and note the weights; the respective figures will represent the relative weights of equal bulks of the liquids. If the capacity of the bottle is 10, 100, or 1000 grains, the resulting weights will, without calculation, show the specific gravities of the liquids; if any other number, a rule-of-three sum must be worked out to ascertain the weight of the liquids as compared with 1 (or 1.000) of water. Bottles conveniently adjusted to

Fig. 66. Fig. 67. Fig. 68. Fig. 69.



Specific-Gravity Bottles.

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* The true weight of the body is its weight in air plus the weight of an equal bulk of air, and minus the weight of a bulk of air equal to the bulk of brass or other weights employed; or, in other words, its weight *in vacuo* uninfluenced by the buoyancy of the air; but such a correction of the weight of a body is seldom necessary, or, indeed, desirable. *Density* is sometimes improperly regarded as synonymous with *specific gravity*. It is true that the density of a body is in exact proportion to its specific gravity, but the former is more correctly the comparative bulk of equal weights, while specific gravity is the comparative weight of equal bulks.

contain 250, 500, or 1000 grains, or 100 or 50 grammes, of water when filled to the top of their perforated stopper (Fig. 68), and other forms of the instrument (Figs. 67 and 69), are sold by all chemical-apparatus makers. Figure 69 is that of a bottle extremely useful in ascertaining the specific gravities of very volatile liquids.

Verify some of the following stated specific gravities of substances official in the U. S. Pharmacopœia, 1880:—

Acid, Acetic	1.048
“ “ dil	1.0083
“ “ Glacial	1.056–1.058
“ Hydrobromic dil	1.077
“ Hydrochloric	1.160
“ “ dil	1.049
“ Lactic	1.212
“ Nitric	1.420
“ “ dil	1.059
“ Oleic	.800–.810
“ Phosphoric	1.347
“ “ dil	1.057
“ Sulphuric	1.840
“ “ Aromat	.955
“ “ dil	1.067
“ Sulphurous	1.022–1.023
Æther	.750
“ Acetic	.889–.897
“ Fortior	.725
Alcohol	.820
“ dil	.928
Amyl Nitris	.872–.874
Aq. Ammon	.959
“ “ Fort	.900
Bals. Peru	1.135–1.150
Benzinum	.670–.675
Bromum	2.990
Camphora	.990–.995
Carbonei Bisulphidum	1.272
Cera Alba	0.965–0.975
Cera Flava	.955–.967
Cetaceum	0.945
Chloroform Purif	1.485–1.490
“ Venali	1.470
Copaiba	.940–.993
Creosote	1.035–1.085
Fel Bovis	1.018–1.028
Glycerinum	1.250
Hydrargyrum	13.5
Iodoformum	2.00
Liq. Ammon. Acet	1.022
Liq. Calcis	1.0015
“ Ferri Acetatis	1.160
“ “ Chloridi	1.405
“ “ Citratis	1.260
“ “ Nitratis	1.050
“ “ Subsulph	1.555
“ “ Tersulph	1.320
“ Hydrarg. Nit	2.100
“ Plumbi Subacetatis	1.228
“ Potassæ	1.036
“ Potassii Citratis	1.059
“ Sodæ	1.059
“ “ Chloratæ	1.044
“ Sodii Silicatis	1.300–1.400
“ Zinci Chlor	1.555
Mel	1.101–1.105
Oleum Adipis	0.900–0.920
“ Æthereum	0.910
“ Amygd. Amar.	1.060–1.070 1.043–1.049
“ “ Express	.914–.920
“ Anisi	.976–.990
“ Aurantii Cort	.860
“ “ Flor	.850–.890
“ Bergamii	.860–.890
“ Cajuputi	.920
“ Cari	.920
“ Caryoph	1.050
“ Chenapodii	.920
“ Cinnamomi (*Ceylon*)	1.040
“ “ (*Chinese*)	1.060
“ Copaiba	.890
“ Coriandri	.870
“ Cubebæ	.920
“ Erigerontis	.850
“ Eucalypti	.900
“ Fœniculi	.960
“ Gaultheriæ	1.180
“ Gossypii Sem	.920–.930
“ Hedeomæ	.940
“ Juniperi	.870

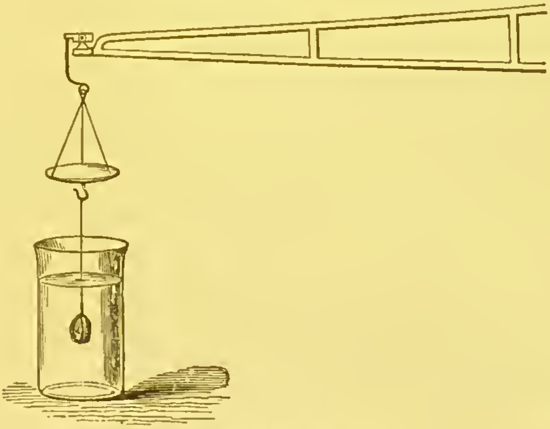
Oleum Lavendulæ	.890	Oleum Succini	.920
“ “ Flor	.890	“ Terebinthinæ	.855–.870
“ Limonis	.850	“ Thymi	.880
“ Lini	.936	“ Tiglii	.940–.955
“ Menth. Pip	.900	“ Valerianæ	950
“ “ Virid	.900	Petrolatum	.835–.860
“ Morrhuæ	.920–.925	Phosphorus (at 50° F.)	1.83
“ Myrciæ	1.040	Resina	1.070–1.080
“ Myristicæ	.930	Sp. Ætheris Nitrosi	.823–.825
“ Olivæ	.915–.918	“ Ammoniæ	.810
“ Picis Liquida	.970	“ Ammoniæ Aromat	.885
“ Pimentæ	1.040	“ Frumenti	.930–.917
“ Ricini	.950–.970	“ Vini Gallici	.941–.925
“ Rosæ	.860	Syrupus	1.310
“ Rosmarini	.900	Syr. Acidi Hydriodici	1.300
“ Rutæ	.880	Thymol	1.028
“ Sabinæ	.910	Tinct. Ferri Acetatis	0.950
“ Santali	.945	“ “ Chloridi	0.980
“ Sassafras	1.090	Vinum Album	.990–1.010
“ Sesami	.914–.923	“ Rubrum	.989–1.010
“ Sinapis Vol	1.017–1.021	Zincum	6.9

Hydrometers.—The specific gravity of liquids may be ascertained without scales and weights by means of a *hydrometer*, an instrument usually of glass, having a graduated stem and a bulb or bulbs at the lower part. The specific gravity of a liquid is indicated by the depth to which the hydrometer sinks in the liquid, the zero of the scale marking the depth to which it sinks in pure water. Hydrometers constructed for special purposes are known under the names of saccharometer, galactometer, elæometer, urinometer, alcoholometer. Hydrometers require a considerable quantity of liquid to fairly float them, and specific gravities observed with them are less delicate and trustworthy than those obtained by the balance; nevertheless, they are exceedingly useful for many practical purposes where the employment of a delicate balance would be inadmissible.

Specific Gravity of Solids in Mass.

Weigh a piece (50 to 250 grains) of any solid substance heavier than water in the usual manner. Then weigh it in water by suspending it from a shortened balance-pan by a fine thread or hair and immersing in a vessel of water (Fig. 70). The buoyant properties of the water will cause the solid apparently to lose weight; *this loss in weight is the exact weight of an equal bulk of water.* The weight of the substance and the weight of an equal bulk of water being thus ascertained, a rule-of-three sum shows the proportional weight of the substance to 1.000 of water. To express the same thing by rule, divide the weight in air by the loss of weight in water; the resulting number is the specific gravity in relation to 1 part of water, the conventional standard of comparison.

Fig. 70.



Weighing a Solid in Water.

Verify some of the following specific gravities:—

Aluminium	2.56	Lead	11.36
Antimony	6.71	Magnesium	1.74
Bismuth	9.83	Marble	·2.70
Coins, English, gold	17.69	Phosphorus	1.77
" " silver	10.30	Platinum	21.53
" " bronze	8.70	Silver	10.53
Copper	8.95	Sulphur	2.05
Gold	19.34	Tin	7.29
Iron	7.84	Zinc	7.14

Specific gravities of solid substances should be taken in water having a temperature of about 15° C. (59° F.). The body should be immersed about half an inch below the surface of the water; adhering air-bubbles must be carefully removed; the body must be quite insoluble in water.

(For a Table of the specific gravities of a large number of fatty and resinoid substances see the *Pharmaceutical Journal* for Oct. 11, 1879.)

SPECIFIC GRAVITY OF SOLIDS IN POWDER OR SMALL FRAGMENTS.

Weigh the particles; place them in a counterpoised specific-gravity bottle of known capacity, and fill up with water, taking care that the substance is thoroughly wetted; again weigh. From the combined weights of water and substance subtract the amount due to the substance; the residue is the weight of the water. Subtract this weight of water from the quantity which the bottle normally contains; the residue is the amount of water displaced by the substance. Having thus obtained the weights of equal bulks of water and substance, a rule-of-three sum shows the relation of the weight of the substance to 1 part of water—the specific gravity.

Or suspend a cup, short glass tube, or bucket from a shortened balance-pan; immerse in water; counterpoise; place the weighed powder in the cup, and proceed as directed for taking the specific gravity of a solid in mass.

This operation may be conducted on fragments of any of the substances the specific gravities of which are given in the foregoing Table, or on a powdered piece of marble the specific gravity of which has been taken in mass. The specific gravity of one piece of glass, first in mass, then in powder, may be ascertained; the result should be identical. The specific gravity of shot is about 11.350; sand, 2.600; mercury, 13.56.

Specific Gravity of Solids Soluble in Water.

Weigh a piece of sugar or other substance soluble in water; suspend it from a balance in the usual manner, and weigh it in turpentine, benzol, or petroleum, the specific gravity of which is known or has been previously determined; the loss in weight is the weight of an equal bulk of the turpentine. Ascertain the weight of an equal bulk of water by calculation:—

Sp. gr. of turpentine : sp. gr. of water :: observed bulk of turp. : equal bulk of water.

The exact weights of equal bulks of sugar and water being obtained, the weight of a bulk of sugar corresponding to 1.000 of water is shown by a rule-of-three sum; in other words, divide the weight of sugar by that of the equal bulk of water: the quotient is the specific gravity of sugar. The stated specific gravity of the sugar ranges from 1.590 to 1.607.

Specific Gravity of Solids Lighter than Water.

This is obtained in a manner similar to that for solids heavier than water; but the light body is sunk by help of a piece of heavy metal, the bulk of water which the latter displaces being deducted from the bulk displaced by both; the remainder is the weight of a bulk of water equal to the bulk of the light body. For instance, a piece of wood weighing 12 grammes (or grains) is tied to a piece of metal weighing 22 grammes, the loss of weight of the metal in water having been previously found to be 3 grammes. The two, weighing 34 grammes, are now immersed, and the loss in weight found to be 26 grammes. But of this loss 3 grammes have been proved to be due to the buoyant action of the water on the lead; the remaining 23 therefore represent the same effect on the wood; 23 and 12 therefore represent the weights of equal bulks of water and wood. As 23 are to 12, so is 1 to .5217. Or, shortly, as before, divide the weight in air by the weight of an equal bulk of water; .5217 is the specific gravity of the wood. Another specimen of wood may be found to be three-fourths (.750) the weight of water, and others heavier. Cork varies from .100 to .300.

Specific Gravity of Gases.

This operation is similar to that for liquids. A globe exhausted of air and holding from 1 to 4 litres (or quarts) is suspended from the arm of a balance, and counterpoised by a similar flask. Gases are introduced in succession and their weights noted. A rule-of-three sum shows their specific gravity in relation to air or hydrogen, whichever be taken as a standard.

Correction of the Volume of Gases for Pressure.—The height of the barometer at the time of manipulation is noted. Remembering the fact that "the bulk of a gas is inversely as the pressure to which it is subjected" (Boyle and Mariotte), a simple calculation shows the volume which the gas would occupy at 760 millimetres (or 29.922 inches), the standard pressure (30 inches is sometimes adopted as the standard in England*). Thus, 40 volumes of a gas at 740 millimetres pressure are reduced to 39 when the pressure becomes 760 millimetres (or 90 vols. at 29 ins. barom. become 87 vols. at 30 inches.)

Correction of the Volume of Gases for Temperature.—This is done in order to ascertain what volume the gas would occupy at 0° C. (32° F.). or 15° C. (59° F.), or 15°.5 C. (60° F.), according to the standard taken. Gases are equally affected by equal variations in temperature (Charles). They expand about 0.3665† per cent. ($\frac{1}{273}$) of their volume *at the freezing-point of water* for every C. degree (0.2036), or

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* In France the conventional standard height of the barometer is 760 millimetres at 0° C. (32° F.); in England it is 30 inches, the temperature of the mercurial column being 60° F. 760 millims. is equivalent to 29.922 inches, but the expansion of the metal between 32° F. and 60° F. increases the length of the column to 30.005 inches. The standards are therefore almost identical, difference in true length being counterbalanced by the temperature at which the length is observed.

† Corrected for the difference between the mercurial and air thermometers, the coefficient of expansion of air is 0.003656 (Miller). The coefficient of expansion of different gases varies very slightly, being somewhat higher for the more liquefiable gases.

$\frac{1}{491}$ for every F. degree (Regnault). Thus, 8 volumes of gas at 0° C. will become 8.293 at 10° C.; for if 100 become 103.665 on being increased in temperature 10° C., 8 will become 8.293 (or if 100 become 102.036 on being increased 10° F., 8 will become 8.1629).

Vapor-Density.—Vapors are those gases which condense to liquids at common temperatures. By the density of a vapor is meant its specific gravity. The density of a vapor is the ratio of any given volume to a similar volume of air or hydrogen at the same temperature and pressure. But for convenience of comparison this experimental specific gravity is referred, by calculation as just described for permanent gases, to a temperature of 0° C. and 760 millimetres barom. A teaspoonful or so of liquid is placed in a weighed flask of about the capacity of a common tumbler and having a capillary neck; the flask is heated in an oil-bath to a temperature considerably above the boiling-point of the liquid; at the moment vapor ceases to escape the neck is sealed by a blowpipe-flame and the temperature of the bath noted; the flask is then removed, cooled, cleaned, and weighed; the height of the barometer is also taken. The neck of the flask is next broken off beneath the surface of water or mercury (which rushes in and fills it), and again weighed, by which its capacity in cub. centims. is found. From these data the volume of vapor yielded by a given weight of liquid is ascertained by a few obvious calculations. The capacity of the globe having been ascertained, the weight of an equal bulk of air* is obtained by a rule-of-three sum. This weight of air is deducted from the original weight of the flask, which gives the true weight of the glass. The weight of the glass is next subtracted from the weight of the flask and contained vapor (now condensed), which gives the weight of material used in the experiment. The volume which this weight of material occupied at the time of experiment is next corrected for temperature (to 0° C.) and pressure (760 millimetres) in the manner just described. The weight of a similar volume of hydrogen is next found.† The weights of equal volumes of hydrogen and vapor being thus determined, the amount of vapor corresponding to one of hydrogen (the specific gravity or vapor-density) is shown by a short calculation. This process of finding the weight of a given volume of vapor is by Dumas. Gay-Lussac's consists in determining the volume of a given weight; it has been improved by Hofmann. An excellent method by V. and C. Meyer consists, like that of Gay-Lussac, in determining the volume of the vapor of a given weight of a fluid or solid, but differs in the volume of the vapor being ascertained from an equal volume of air which the vapor is made to displace. (For a detailed description of this method and a drawing of the apparatus see *Pharmaceutical Journal*, May 17, 1879.)

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* 1 cub. centim. of air at 0° C. and 760 millims. weighs 0.001293 gramme.

† 1 litre (1000 cub. centims.) of hydrogen at 0° C. and 760 millimetres (the barometer being at 0° C.) weighs 0.0896 gramme—a quantity sometimes termed a *crith* (from κριθή, *krithē*, a barley-corn—figuratively, a small weight); thus a litre of oxygen weighs 16 criths, chlorine 35.5 criths, etc. 100 cubic inches of hydrogen at 32° F. weigh 2.265 grains; at 60° F., 2.143 grains (the barometer being 30 ins. at 60° F. in both cases). 100 cubic inches of air at 32° F. weigh 32.698 grains; at 60° F., 30.935 (barom. 30 ins. at 60° F.). 1 cubic inch of water weighs 252.5 (252.458 at 62° F. and 30 ins. bar.) grains. 1 gallon of water contains 277¼ (277.274 at 62° F.) cubic inches.

Experiment shows that the specific gravities of many gases and vapors on the hydrogen scale, and the proportions in which they combine by weight, are identical. Thus, chlorine is 35.5 times as heavy as hydrogen, and 35.5 parts unite with 1 of hydrogen to form hydrochloric acid gas. Hence, if the specific gravity of a gas or vapor is known, its combining proportion may be predicated with reasonable certainty, and *vice versâ*. In applying this rule to gaseous or vaporous compounds attention must be paid to the extent to which their constituent gases contract at the moment of combination or expand at the moment of decomposition. Thus, steam is found to be composed of two volumes of hydrogen and one of oxygen, the three volumes of constituents condensing to two at the moment of combination. Hence, steam may be expected to be nine times as heavy as hydrogen; which experiment confirms.

These relations may be so expressed as to include both elementary and compound gases and vapors; thus, *molecular weights and specific weights are identical.* Molecular weights represent two volumes of a gas; specific gravity conventionally represents the relative weight of a gas compared with 1 volume of hydrogen or air; hence the specific gravity of a gas or vapor on the H scale is found by calculation on simply dividing the molecular weight by 2; on the air-scale, by dividing the hydrogen numbers by 14.44. For example,

Name.	Molecular formula.	Molecular weight.	Specific Gravity.		
			H = 2.	H = 1.	Air = 1.
Hydrogen	H_2	2	2	1	.069
Chlorine	Cl_2	71	71	35.5	2.460
Oxygen	O_2	32	32	16	1.108
Nitrogen	N_2	28	28	14	.970
Steam	H_2O	18	18	9	.625
Ammonia gas . .	NH_3	17	17	8.5	.589
Carbonic acid gas .	CO_2	44	44	22	1.524
Alcohol (vapor) .	C_2H_6O	46	46	23	1.593
Air		. .	28.88	14.44	1.000

These specific gravities closely correspond with those obtained by actual experiment. The specific gravity of any gas or vapor may therefore be calculated if the following data are at hand: (*a*) formula, (*b*) atomic weight of constituent elements; these give the molecular weight, and *the molecular weight divided by 2 is the specific gravity* on the hydrogen-scale. Specific gravity on the air-scale is then deducible, if (*c*) the specific gravity of air (14.44) in relation to hydrogen be remembered. The absolute weight of any volume of a gas or vapor on the metric system is then obtainable if (*d*) the weight of a litre of hydrogen (0.0896 gramme) be known, or on the English plan by remembering (*e*) that 100 cubic inches of hydrogen at 60° F. weigh 2.143 grains (100 cubic inches of air at 60° F. weigh 30.935 grains).

In confirmation of these statements regarding the mutual relation of specific gravity and atomic weight a remarkable fact may be mentioned. Regnault several years ago found the weights of 1 litre of hydrogen and oxygen to be respectively .089578 and 1.429802 grammes. The latter number divided by the former gives 15.96 as the specific gravity of oxygen. Stas, in recent experimental researches on combining proportions, finds the atomic weight of oxygen to be not 16, but 15.96.

Exceptions to the law occur in a few compounds and in arsenicum and phosphorus, whose vapor-densities are twice that indicated by the rule. Possibly, in these cases the temperature employed is insufficient to dissociate an unusually complex molecule into molecules of usual complexity. As regards compounds, and, possibly, as regards those elements in which the observed density is only half that indicated by the rule, heat may, and in some cases probably does, produce molecular *dissociation* (*thermolysis*) into free atoms (uniatomic molecules) or into less complex molecules.

Relation of the Specific Heat of Elements to their Atomic Weights.—Reference may here appropriately be made to a physical fact of great importance as regards molecular and atomic weights. In the earlier pages of this manual it was stated that elements do not combine chemically in haphazard proportions, but in fixed weights; and abundant evidence of the truth of the statement has already been afforded, and will also be found in this section on Quantitative Analysis. Secondly, it has been shown that elements do not combine in haphazard proportions by volume, but in certain constant bulks; and the weights of these bulks have been found to be identical with the combining weights themselves. Thirdly (this is the point to which attention is now drawn), if equal amounts of heat be given to elements in the solid state (that is, to solid elements or to solid compounds of volatile elements), and the quantity of the element be increased or diminished until each is thus heated through an equal number of degrees, it will be found that the different weights of elements required are (in relation to a common standard) identical with the combining weights of the elements and with the weights of the combining volume of the elements. Thus, where 108 parts of silver would be employed, 207 of lead would be necessary.* Hence, in the determination of (*a*) combining proportion, (*b*) specific gravity in gaseous state, and (*c*) specific heat, three distinct methods of ascertaining atomic weight are available. In cases where one method is inapplicable, recourse is had to either, or, if practicable, both, of the others, and thus the trustworthiness of observations and generalizations placed more or less beyond question. The specific heat of a solid element is the same in the free as in the combined condition; therefore the specific heat of a molecule is the sum of the specific heat of its constituent atoms. From the specific heat of a solid compound of a volatile element (chlorine, for example) can thus be calculated the specific heat of an element in the solid state, even though the free element cannot itself be solidified. For the processes by which experimentally to determine specific heat the reader is referred to books on Physics.

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* Obviously, if equal weights of silver and lead were heated through an equal number of degrees, the silver would absorb nearly twice as much heat as the lead. In fact, as regards all the solid elements, "specific heats and atomic weights are inversely proportional." This law was discovered by Dulong and Petit. It follows that the product of the multiplication of the figures representing the specific heat of an element with the figures representing its atomic weight is, in the case of every such element, the same number.

There is equivalency, also, between electrical and chemical action. The amount of electricity which would set free 127 parts of iodine would set free 80 parts of bromine.

QUESTIONS AND EXERCISES.

971. Define specific weight, or, as it is commonly termed, specific gravity.

972. In speaking of light and heavy bodies especially, what standard of comparison is conventionally employed?

973. How are specific gravities expressed in figures?

974. Why should specific gravities be taken at one constant temperature?

975. How does the buoyancy of air affect the real weight of any material?

976. Describe the difference between density and specific gravity.

977. Give a direct method for the determination of the specific gravity of liquids.

978. A certain bottle holds 150 parts, by weight, of water or 135.7 of spirit of wine; what is the specific gravity of the latter? *Ans.* 0.9046.

978*a*. An imperial fluidounce of a liquid weighs 366½ grains; what is its specific gravity? *Ans.* .838.

979. Equal volumes of benzol and glycerin weigh 34 and 49 parts respectively, and the sp. gr. of the benzol is 0.850; what is the specific gravity of the glycerin? *Ans.* 1.225.

980. Explain the process employed in taking the specific gravity of solid substances in mass and in powder.

981. State the method by which the specific gravity of a light body, such as cork, is obtained.

982. What modifications of the usual method are necessary in ascertaining the specific gravity of substances soluble in water?

983. How is the specific gravity of gases determined?

984. By what law can the volume of a gas at any required pressure be deduced from its observed volume at another pressure?

985. To what extent will 78 volumes of a gas at 22.3 inches barometer alter in bulk when the pressure, as indicated by the barometer, is 30.2 inches?

986. Write a short account of the means by which the volumes of gases are corrected for temperature.

987. At the temperature of 15° C. 40 volumes (litres, pints, ounces, cubic feet, or other quantity) of a gas are measured. To what extent will this amount of gas contract on being cooled to the freezing-point of water (0°·C.)?

Answer. As 1 vol. of any gas *at zero* expands or contracts .003665 of a vol. for each rise or fall of 1° C., 1 vol. at 0° C., if heated to 15° C., will become increased by .054975 (that is .003665 multiplied by 15); 1 vol. will expand to 1.054975. Conversely, 1.054975 vol. will contract to 1 vol. if cooled from 15° C. to 0° C. And if 1.054975 becomes 1 in cooling through 15° C., 40 vols. will (as found by rule of three) contract to 37.916.

The following five problems and solutions are from Williamson's *Chemistry*:—

988. 10 litres of oxygen are measured off at 14° F. Required the volume of the gas at 15° C.

Answer. The first operation must be to reduce the temperature quoted in Fahrenheit's degrees to an equivalent value on the Centigrade scale. 14° F. is 18° below 32° F., the freezing-point of water, and a range of 9° on the Fahrenheit scale is equal to a range of 5° on the Centigrade scale, so that the temperature at which the oxygen is measured off is —10° C. The rise of temperature up to 0° expands the gas in such proportion that its volume at 0° is to its volume at —10 as 1 is to 1 —0.03665; *i. e.* as 1 to 0.96335. The further rise of temperature from 0° C. to 15° expands the gas in the proportion of 1 to $1 + 15 \times 0.003665$; *i. e.* 1 to 1.054975. The total rise of temperature therefore expands the gas in the proportion of of 0.96335 to 1.054975.

$$0.96335 : 1.054975 :: 10 : x;$$

$$\therefore x = \frac{10 \times 1.054975}{0.96335} = 10.95.$$

989. 230 cubic centimetres of oxygen are measured off at 14° C. and 740 millimetres mercurial pressure. Required the volume of the gas at the normal temperature and pressure (0° C. and 760 millimetres).

Answer. Let the reduction for change of temperature be made first. The proportion

$$1 + (14 \times 0.003665) : 1 :: 230 : x$$

gives

$$x = \frac{230}{1.05131} = 218.774.$$

To reduce this volume of 740 millimetres pressure to the volume corresponding to the pressure of 760 millimetres, we have the proportion

$$38 : 37 :: 218.77 : x;$$

whence

$$x = \frac{37 \times 218.77}{38} = 213.02.$$

990. A litre of oxygen is confined in a glass flask at 10° C. by the atmospheric pressure, added to that of a column of mercury 60 millimetres high. The flask must be heated to 300° C. without any increase of volume taking place in the oxygen. How high must the column of mercury then be which presses on the gas, supposing the atmospheric pressure to remain constant at 760 millimetres?

Answer. The oxygen is given at 10° C. and 820 millimetres pressure. If the pressure remained constant, the rise of temperature from 10° C. to 300° C. would expand the gas in such proportion that 1.03665 volumes would expand to 2.0995 volumes. In order to prevent any expansion the pressure must be increased in the same proportion, whence

$$1.03665 : 2.0995 :: 820 : x;$$
$$\therefore x = \frac{820 \times 2.0995}{1.03665} = 1660.6.$$

From this total pressure the atmospheric pressure of 760 millimetres has to be deducted, leaving 900.6 millimetres as the height of the required mercurial column.

991. A litre of oxygen is required of the density of 100 at 0° C. What weight of potassic chlorate must be used for its preparation, and what total pressure must be applied to it?

Answer. The pressure required to compress oxygen from the density of 16 to that of 100 is found by the proportion

$$16 : 100 :: 760 : x;$$
$$\therefore x = \frac{76000}{16} = 4750.$$

At the pressure of 4750 millimetres of mercury the weight of a litre of oxygen (16 grammes measure 11.2 litres at 0° C. and 760 millims. pressure) is found by the proportion

$$760 : 4750 :: \frac{16}{11.2} : x;$$

whence

$$x = \frac{16 \times 4750}{11.2 \times 760} = 8.93 \text{ grammes.}$$

The weight of chlorate required for the evolution of 8.93 grammes of oxygen is found from the proportion

$$48 : 122.5 :: 8.93 : x;$$
$$\therefore x = 22.8 \text{ grammes.}$$

992. What is the volume of 12 grammes of hydrogen at 15° C?

Answer. One gramme of hydrogen measures 11.2 litres at 0° C.; therefore 12 grammes measure $12 \times 11.2 = 134.4$ litres at 0°. To find their volume at 15° C. we have the proportion

$$1 : 1 + 15 \times 0.003665 :: 134.4 : x;$$

whence

$$x = 134.4 \times 1.054975 = 141.788 \text{ litres.}$$

993. What interest for chemists have the specific heats of substances?

VOLUMETRIC QUANTITATIVE ANALYSIS.

Preliminary Note.—Great care should be observed in selecting a *fair* sample of any bulk of material that is to be examined either by volumetric or gravimetric quantitative analysis. If the whole quantity is in separate parcels, and there is any ground for believing that the parcels differ in quality, they should, if practicable. be carefully mixed, or, technically, "bulked." Small portions should be taken from different parts of the resulting heap and well mixed in a mortar or other vessel, or in certain cases dissolved and the solution well stirred or shaken. A specimen of the powder or a portion of the solution may then be selected for analysis.

Introduction.—The operations of volumetric analysis consist (*a*) in carrying out some definite *chemical reaction*, already well known to the operator, with (*b*) *definite quantities* of chemicals or salts; (*c*) the exact termination of the reaction between the two salts or chemicals being ascertained—usually by some *chemical indicator* (litmus, starch, etc.). A portion of the chemical or salt, etc. to be tested is carefully weighed. To this is gradually added the second chemical or salt contained in the testing-fluid, commonly termed the Standard Volumetric Solution. The usefulness and, indeed, the preparation, of this Standard Solution is founded (as already indicated on page 521) on some accurate initial gravimetric operation. A *weighed* amount of a pure salt is dissolved in a given *volume* of water. "Accurately *measured* quantities of such a Standard Volumetric Solution will obviously contain just as definite amounts of the dissolved salt as if those amounts were actually *weighed* in a balance, and, as measuring occupies less time than weighing, the volumetric operations can be conducted with great economy of time as compared with the corresponding gravimetric operations."

APPARATUS.

The only special vessels necessary in volumetric quantitative operations are—1. A *litre flask* (Fig. 72), which, when filled to a mark on the neck, contains at 15° C., or about 60° F., one litre (1000 cubic centimetres—*i. e.* 1000 grammes of water*); it serves for preparing solutions in quantities of one litre. 2. A tall cylindrical *graduated litre jar* (Fig. 71) divided into 100 equal parts: it serves for the measurement and admixture of decimal or centesimal parts of a litre. 3. A graduated tube or *burette* (Fig. 73), which, when filled to 0, holds 100 cubic centimetres (a decilitre), and is divided into 100 equal parts; it is used for accurately measuring small volumes of liquids.

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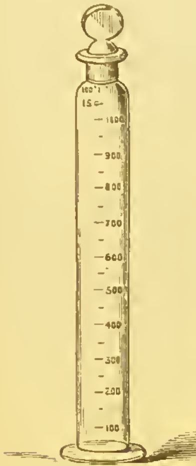
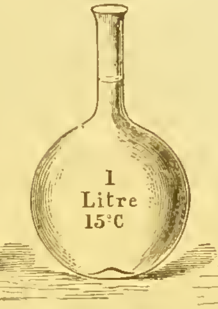
* A cubic centimetre is, strictly speaking, the volume occupied by one gramme of distilled water at its point of greatest density—namely, 4° C.; metrical measurements, however, are uniformly taken at 15°.55 C. (60° F.).

Fig. 71.



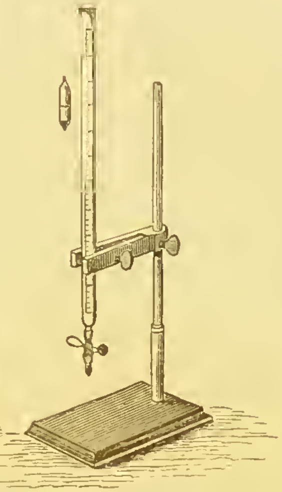
A litre jar.

Fig. 72.



A litre flask.

Fig. 73.



A burette, etc.

The best form of burette is Mohr's. It consists of a glass tube, commonly about the width of a little finger and the length of an arm from the elbow, contracted at the lower extremity and graduated. The width and length of burettes, however, as well as the extent and fineness of their graduation, vary considerably. To the contracted portion is fitted a small piece of vulcanized caoutchouc tubing, into the other end of which a small spout made of narrow glass tube is tightly inserted. A strong wire clamp effectually prevents any liquid from passing out of the burette unless the knobs of the clamp are pressed by the finger and thumb of the operator, when a stream or drops flow at will. In place of the India-rubber tubing and clamp a stopcock is sometimes employed, and other modes of arresting the flow of liquid may be adopted. The accurate reading of the height of a solution in the burette is a matter of great importance; it should be taken from the bottom of the curved surface of the liquid. It may be still more exactly measured by the employment of a hollow glass float or bulb (Erdmann's float: see Fig. 73), of such a width that it can move freely in the tube without undue friction, and so adjusted in weight that it shall sink to more than half its length in any ordinary liquid. A fine line is scratched round the centre of the float; this line must always be regarded as marking the height of the fluid in the burette. In charging the burette a solution is poured in, not until its surface is coincident with 0, but until the mark on the float is coincident with 0.

ESTIMATION OF ALKALIES, ETC.

Volumetric Solution of Oxalic Acid.

(Crystallized Oxalic Acid, $H_2C_2O_4,2H_2O = 126$.)

On account of the bivalent character of the oxalic radical, and the univalent character of most of the metals contained in the salts which are estimated by oxalic acid, it is convenient that each litre of the volumetric solution should contain half a molecular weight in grammes of the acid ($H_2C_2O_4,2H_2O = 126 \div 2 = 63$).

If pure crystallized oxalic acid be at hand, the solution is made by dissolving 63 grammes in water, and making the volume up with more water to exactly one litre.

Pure oxalic acid, however, not being easy to obtain, the solution may be made from the commercial acid by dissolving 65 to 70 grammes in enough water to make a litre of solution, and then determining the strength of this solution by a titration with pure carbonate of sodium, making use of the following memoranda:—

$$\underbrace{Na_2CO_3}_{2)\underline{106}\ 53} + \underbrace{H_2C_2O_4,2H_2O}_{2)\underline{126}\ 63} = Na_2C_2O_4 + CO_2 + 3H_2O$$

Pure anhydrous carbonate of sodium is easy to obtain, for commercial bicarbonate is usually of such purity that when a few grammes are heated to redness for a quarter of an hour the resulting carbonate is practically free from impurity. The bicarbonate should, however, be tested, and if more than traces of chlorides and sulphates are present, these may be removed by washing a few hundred grammes, first with a saturated solution of bicarbonate of sodium, and afterward with pure distilled water. After drying, the salt is ready for ignition.

About half a gramme of the carbonate of sodium is accurately weighed and placed in a half-pint flask, around the neck of which is tied calico or leather to protect the fingers when the heated vessel is shaken by the operator. The salt is dissolved in water to about one-third the capacity of the flask, and a few drops of the indicator, blue tincture of litmus, is added. The acid solution to be "set" or "standardized" is then poured into a burette, and run therefrom into the flask until the reddened litmus indicates the presence of free acid. This will be due in the first place to carbonic acid liberated and remaining dissolved in the solution. The contents of the flask are therefore boiled for several minutes, when the blue color will have returned. More acid is then run in until the mixture, after boiling, remains of a neutral color, indicating that just enough acid has been added to complete the reaction expressed in the foregoing equation.

Let it be supposed that 0.6 gramme of carbonate of sodium was taken, and that this required 11 c.c. of oxalic acid solution; how many c.c. of this solution would contain 63 grammes of oxalic acid crystals? or, what is equivalent in the reaction, how many c.c. would be required to neutralize 53 grammes of carbonate of sodium? As 0.6 gramme Na_2CO_3 is to 11 c.c. sol., so are 53 grammes Na_2CO_3 to x c.c. sol.; $x = 972$ c.c. 972 c.c. (nearly) are equivalent to 53 grammes of carbonate of sodium, and contain 63 grammes of oxalic acid.

This solution may either be used as it is, or may be diluted with water, every 972 c.c. to be diluted to 1000 c.c., so that 1000 c.c. shall contain 63 grammes of oxalic acid.

The following official substances are tested by this solution according to the United States Pharmacopœia:—

Solutions of Ammonia.—2 or 3 grammes of dilute, or about 1 gramme of strong, solution of ammonia is a convenient quantity to operate upon. The weighing is most conveniently accomplished by taking a small stoppered bottle containing half an ounce or so of the substance, and, having ascertained its total weight, transfer about the quantity desired to the flask in which the estimation is to be conducted, and again weigh the bottle with what remains in it. The difference is the exact quantity taken. The weighing of the ammonia solution having been accomplished, water is added to about one-third the capacity of the flask (or, better, the ammonia is added to water already in the flask), and a few drops of tincture of litmus introduced. The titration is then conducted as described before, except that no heat is employed.

$$\underbrace{2NH_4HO}_{\substack{2)\underline{70}\\35}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)\underline{126}\\63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = (NH_4)_2C_2O_4 + 4H_2O$$

$$\underbrace{2NH_3H_2O}_{\substack{2)\underline{34}\\17}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)\underline{126}\\63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = (NH_4)_2C_2O_4 + 4H_2O$$

1000 c.c. of standard solution, or its equivalent of a solution of any other strength, would, according to this reaction, neutralize 17 grammes of ammonia gas (NH_3) or 35 grammes of hydrate of ammonium (NH_4HO). If 3 grammes of ammonia solution had been taken, and it had required 15 c.c. of standard oxalic acid solution, then the amount of ammonia gas or hydrate of ammonium it contained would be seen by the following calculations:—

1000 c.c. : $17NH_3$: : 15 c.c. : $x = .255$ grammes NH_3
1000 c.c. : $35NH_4HO$: : 15 c.c. : $x = .525$ grammes NH_4HO

Three grammes, then, would contain .255 grammes of the gas or .525 grammes of hydrate of ammonium. Or, in percentage,

3 gr. sol. : .255 gr. NH_3 : : 100 gr. sol. : x gr. NH_3 = 8.5% NH_3
3 gr. sol. : .525 gr. NH_4HO : : 100 gr. sol. : x gr. NH_4HO = 17.5% NH_4HO

The solution would therefore contain 8.5 per cent. of ammonia gas (NH_3) or 17.5 per cent. of hydrate of ammonium (NH_4HO). If the oxalic acid solution was not of full standard, the number of c.c. which contained 63 grammes of oxalic acid—which was, in fact, equivalent to 1000 c.c. of standard solution—would be substituted for 1000 c.c. in the preceding proportions.

A comparison should now be made with the requirements of the Pharmacopœia. It is useful to express results as percentage of substance of pharmacopœial strength in the material examined. Thus the U. S. Pharmacopœia requires dilute ammonia solution (both *Aqua Ammoniæ* and *Spiritus Ammoniæ*) to contain 10 per cent. of the gas (NH_3). The solution supposed to have been operated on contained 8.5 per cent. NH_3 ($10 : 8.5 :: 100 : x = 85$). Therefore it contains 85 per cent. of the dilute ammonia of the U. S. Pharmacopœia.*

Strong Solution of Ammonia, U. S. P., contains 28 per cent. of ammonia gas (NH_3).

Note.—The calculations just described for ammonia are similar to those employed throughout volumetric analysis; they will not be repeated, therefore, in the case of every substance.

Carbonate of Ammonium.—The reactions indicated by the following equations occur between commercial carbonate of ammonium and oxalic acid:—

$$\underbrace{2N_3H_{11}C_2O_5}_{\substack{6)314\\ 52.33}} + \underbrace{3H_2C_2O_4,2H_2O}_{\substack{6)378\\ 63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = 3(NH_4)_2C_2O_4 + 8H_2O + 4CO_2$$

About 1 gramme is a convenient quantity to operate upon. Tincture of litmus is the indicator, and the titration is conducted at a temperature just short of boiling. The estimation is not very satisfactory, because the heat employed, while scarcely sufficient to expel the carbonic acid gas, is enough to occasion loss of ammoniacal salt. Practised analysts usually add excess of the standard acid, and thus

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* Extremely minute quantities of ammonia—1 part in many millions of water—may be estimated volumetrically by adding excess of a colorless solution of red iodide of mercury (Nessler's test), then in a similar vessel, containing an equal amount of pure water with excess of the Nessler reagent, imitating the depth of yellow or reddish-yellow color thus produced by adding an ammoniacal solution *of known strength*. The amount of ammonia thus added represents the amount in the original liquid.

The Nessler Reagent.—A litre may be made by dissolving 30 or 40 grammes of iodide of potassium in a small quantity of hot water, adding a strong hot solution of perchloride of mercury until the precipitate of mercuric iodide ceases to redissolve even by the aid of rapid stirring and heat, slightly diluting, filtering, adding a strong solution of (120 to 140 grammes) caustic soda or (160 to 180 grammes) caustic potash, and diluting to 1 litre. A few c.c. (5 or 6 or more) of a strong solution of perchloride of mercury are finally stirred in, the whole set aside till all precipitated red iodide has deposited, and the clear liquid decanted for use. The reaction of this Nessler test with ammonia is as follows:—

$$NH_3 + 2HgI_2 + 3KHO = NHg_2I + 3KI + 3H_2O.$$

fix every trace of ammonia; then gently boil to get rid of carbonic acid gas; bring back the liquid to neutrality by an observed volume of standard alkaline solution, and deduct an equivalent volume of acid from the quantity first added. The United States Pharmacopœia requires 5.232 grammes to neutralize 100 c.c. of standard solution of oxalic acid. This corresponds to 100 per cent. of carbonate having the formula $N_3H_{11}C_2O_5$.

Borax.—Two or three grammes is a convenient quantity.

$$\underbrace{Na_2B_4O_7,10H_2O}_{\substack{2)382\\ 191}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ 63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = Na_2C_2O_4 + H_2B_4O_7 + 12H_2O$$

Tincture of litmus is the indicator, and the titration may be carried on without heat. The liberation of boracic acid colors the litmus wine-red. This is not regarded, the titration being continued until the bright red due to the action of free oxalic acid makes its appearance. Both the British and United States Pharmacopœias require borax to be pure (= 100 per cent.).

Lead Acetate and Solution of Subacetate.—Operate upon about three grammes of acetate of lead and from five to ten grammes of solution of subacetate.

$$\underbrace{Pb2C_2H_3O_2,3H_2O}_{\substack{2)378.5\\ 189.25}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ 63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = PbC_2O_4 + 2HC_2H_3O_2 + 5H_2O$$

$$\underbrace{Pb_2O2C_2H_3O_2}_{\substack{4)547\\ 136.75}} + \underbrace{2(H_2C_2O_4,2H_2O)}_{\substack{4)252\\ 63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = 2PbC_2O_4 + 2HC_2H_3O_2 + 5H_2O$$

The flask in which the estimation is being conducted should contain one third of a flaskful of water. In the case of both acetate and solution of subacetate of lead a little acetic acid should be added to prevent precipitation of basic salt on dilution. The only indicator of complete reaction is cessation of production of the precipitate—oxalate of lead. The United States Pharmacopœia requires acetate of lead to be pure (100 per cent.), and solution of subacetate to contain 25 per cent.

Lime-Water and Saccharated Solution of Lime.—Measure about half a litre of lime-water for the estimation, and of saccharated solution weigh about 25 grammes. The following equations, etc. are quantitative expressions of the reactions:—

$$\underbrace{Ca2HO}_{\substack{2)74\\ 37}} + \underbrace{H_2C_2O_4}_{\substack{2)126\\ 63\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = CaC_2O_4 + 2H_2O$$

Or,

$$\underbrace{CaO,H_2O}_{\substack{2)56\\28}} + \underbrace{H_2C_2O_4}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = CaC_2O_4 + 2H_2O$$

Litmus is used as an indicator.

Caustic Potash and Soda, Potassium and Sodium Carbonates and Bicarbonates.—Litmus is the indicator throughout, and heat is used in all cases, for the caustic alkalies always contain some carbonate.

$$\underbrace{2KHO}_{\substack{2)112\\56}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = K_2C_2O_4 + 4H_2O$$

$$\underbrace{2NaHO}_{\substack{2)80\\40}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = Na_2C_2O_4 + 4H_2O$$

$$\underbrace{K_2CO_3}_{\substack{2)138\\69}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = K_2C_2O_4 + CO_2 + 3H_2O$$

Or,

$$\underbrace{K_2CO_3 + 16\% H_2O}_{\substack{2)164.28\\82.14}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = K_2C_2O_4 + CO_2 + xH_2O$$

$$\underbrace{Na_2CO_3}_{\substack{2)106\\53}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = Na_2C_2O_4 + CO_2 + 3H_2O$$

Or,

$$\underbrace{Na_2CO_3,10H_2O}_{\substack{2)286\\143}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = Na_2C_2O_4 + CO_2 + 13H_2O$$

$$\underbrace{2KHCO_3}_{\substack{2)200\\100}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = K_2C_2O_4 + 2CO_2 + 4H_2O$$

$$\underbrace{2NaHCO_3}_{\substack{2)168\\84}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\63 = \text{grammes in 1000 c.c. of standard solution.}}} = Na_2C_2O_4 + 2CO_2 + 4H_2O$$

Convenient quantities to operate with are: Of caustic potash, 1 gramme; caustic soda, .5 to 1 gramme; potassium carbonate or bicarbonate, 1 to 2 grammes; sodium carbonate or bicarbonate, 2 to 3 grammes; dried sodium carbonate, .5 to 1 gramme; and of solutions a corresponding quantity. The United States Pharmacopœial requirements are: Caustic potash or soda, 90 per cent. of KHO or NaHO; potassium carbonate, 81 per cent. of K_2CO_3; sodium carbonate, 98 per cent. of $Na_2CO_3,10H_2O$; potassium bicarbonate, 100 per cent. of $KHCO_3$; sodium bicarbonate, 99 per cent. of $NaHCO_3$; and commercial bicarbonate, at least 95 per cent. The dried carbonate (*Sodii Carbonas Exsiccatus*, U. S. P.) is to contain 72.6 per cent. of real carbonate. *Liquor Potassæ* and *Liquor Sodæ* must contain 5 per cent. of pure hydrate.

The strength of soda-ash is often reported in terms of "soda"—that is, oxide of sodium ($Na_2O = 62$). The old molecular weight of carbonate of sodium, 54 (it should have been 53), derived from that of "soda," 32 (it should have been 31), is still employed in Great Britain in reporting the strength of soda-ash. The true amount of soda equivalent to 54 parts of carbonate is 31.41 parts. A modern analyst having found the true amount of soda in a sample of soda-ash is expected by some manufacturers to report 31 as 31.41 parts, or 53 of carbonate as 54, and other quantities in proportion to these figures.

Tartrates and Citrates of Potassium and Sodium and Acetate of Potassium.—When tartrates or citrates of alkali-metals are burned in the open air the whole of the metal remains in the form of carbonate. Each molecular weight of a neutral tartrate gives one molecular weight of carbonate, and every two molecular weights of an acid tartrate give one molecular weight of carbonate. Advantage is taken of these reactions to estimate indirectly the quantity of citrate or tartrate in presence of substances with which they are generally associated. One to two grammes of any of these salts is a convenient quantity to operate upon. The ignition may be conducted in a platinum or porcelain crucible. A low red heat only should be used, and the vessel removed when complete carbonization has been effected—that is to say, when nothing remains but the carbonate and free carbon. The mixture is in this case treated with hot water, and the carbon separated by filtration. If too little heat has been used and carbonization is not complete, the filtrate will be more or less colored. If this should be the case the operation must be repeated with a fresh quantity of material. The carbonate is titrated in the usual way. The following equations, etc. explain the reactions:—

$$\underbrace{2K_2C_4H_4O_6,H_2O}_{4)470} + 5O_2 = \underbrace{2K_2CO_3}_{4)276} + 6CO_2 + 4H_2O$$

117.5 69 = 1000 c.c. of standard oxalic acid solution.

$$\underbrace{2KHC_4H_4O_6}_{2)376} + 5O_2 = \underbrace{K_2CO_3}_{2)138} + 7CO_2 + 5H_2O$$

188 69 = 1000 c.c. of standard oxalic acid solution.

$$\underbrace{2(K_3C_6H_5O_7,H_2O)}_{\substack{6)\underline{648}\\108}} + 9O_2 = \underbrace{3K_2CO_3}_{\substack{6)\underline{414}\\69 = \text{to 1000 c.c. of standard oxalic acid solution.}}} + 9CO_2 + 7H_2O$$

$$\underbrace{2(KNaC_4H_4O_6,4H_2O)}_{\substack{4)\underline{564}\\141}} + 5O_2 = \underbrace{2KNaCO_3}_{\substack{4)\underline{244}\\61 = \text{1000 c.c. of standard oxalic acid sol.}}} + 6CO_2 + 8H_2O$$

$$\underbrace{2KC_2H_3O_2}_{\substack{2)\underline{196}\\98}} + 4O_2 = \underbrace{K_2CO_3}_{\substack{2)\underline{138}\\69 = \text{1000 c.c. of standard oxalic acid solution.}}} + 3CO_2 + 3H_2O$$

It will be readily understood that in the first (for example) of the reactions just expressed 113 weights of tartrate of potassium are equivalent to 69 weights of carbonate of potassium; and as in a previous reaction it has been shown that 69 weights of carbonate of potassium are equivalent to 63 weights of oxalic acid, it follows that 113 weights of tartrate of potassium are equivalent to 63 weights of oxalic acid. Let these weights be grammes, and then 113 grammes of tartrate of potassium are equivalent to 63 grammes of oxalic acid, or to 1000 c.c. of the standard solution of oxalic acid. If the substance estimated be a crude sample of tartrate of potassium, and the number of c.c. of oxalic acid used has been 15 c.c., then as 1000 c.c. of the acid solution are to 113 grammes of tartrate of potassium, so are 15 c.c. of the solution to 1.695 grammes of tartrate of potassium. Now, if the weight of the sample taken was 2 grammes, then as 2 grammes of the sample contain 1.695 of real tartrate of potassium, 100 will contain $x = 84.75$ per cent. of real tartrate. These salts are required to be 100 per cent. pure by the United States Pharmacopœia, except acetate of potassium, which is to have 98 per cent. of real acetate. Trade samples are practically pure as a rule.

Permanganate of Potassium.—The reaction is shown in the following equation: $K_2Mn_2O_8 + 3H_2SO_4 + 5(H_2C_2O_4,2H_2O) = K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2$.

$$\underbrace{K_2Mn_2O_8}_{\substack{10)\underline{314}\\31.4}} \text{ and } \underbrace{5(H_2C_2O_4,2H_2O)}_{\substack{10)\underline{630}\\63 = \text{grammes in 1000 c.c. of standard solution.}}}$$

The salt satisfies official requirements if it contains 98.8 per cent. of real permanganate of potassium.

Notes.

Alkalimetry.—The foregoing processes are often spoken of as those of *alkalimetry* (the measurement of alkalies).

Neutral solution of litmus is prepared by digesting the commercial fragments in about 15 or 20 times their weight of water for a few hours, decanting, dividing into two equal portions, adding acid to one till it is faintly red, then pouring in the other and mixing. The solution may be kept in a stoppered bottle and occasionally exposed to the air. It should never be filtered, but gradually allowed to deposit.

Standard sulphuric acid may be used in the place of oxalic acid, 1000 c.c. of the liquid containing half of the molecular weight of the pure acid in grammes. It is prepared by diluting oil of vitriol with from 3 to 4 times its bulk of distilled water, ascertaining how much of the acid liquid is required to exactly neutralize $\frac{1}{20}$ of the molecular weight of pure carbonate of sodium, taken in grammes (5.3), and adding water until the observed volume of acid is increased to 100 c.c., the whole of the fluid being similarly diluted.

Weighing.—In the case of substances which are liable to alter by exposure to air it is important that a selected quantity should be quickly weighed, rather than selected weights be accurately balanced by material, the former operation occupying much the shorter time.

Salts other than the official may be quantitatively analyzed by the volumetric solutions of the Pharmacopœia, slight modifications of manipulation even enabling the processes to be adapted to fresh classes of salts. Ample instructions for extending operations in this manner will be found in Sutton's *Handbook of Volumetric Analysis.*

QUESTIONS AND EXERCISES.

990. Describe the various pieces of apparatus used in volumetric determinations.

991. One hundred cubic centimetres of solution of oxalic acid contain 6.3 grammes of the crystallized acid; work sums showing what weights of bicarbonate of potassium and anhydrous carbonate of sodium that volume will saturate. *Ans.* 10 grammes and 5.3 grammes.

992. Show what weight of hydrate of potassium is contained in solution of potash, 48.02 grammes of which are saturated by 50 c.c. of the standard solution of oxalic acid. *Ans.* 5.83 per cent.

993. Calculate the percentage of hydrate of calcium in lime-water, 438 grammes of which are neutralized by 20 c.c. of the volumetric solution of oxalic acid. *Ans.* 0.1689.

994. Eight grammes of a sample of Rochelle salt, after ignition, etc., require 54.3 c.c. of the official oxalic acid solution for complete saturation; work sums showing what is the centesimal proportion of real salt present. *Ans.* 95.7.

ESTIMATION OF ACIDS.

In the previous experiments a known amount of an acid has been used in determining unknown amounts of alkalies. In those about to be described a known amount of an alkali is employed in estimating unknown amounts of acids. The alkaline salt selected may be either a hydrate or a carbonate; but the former is to be preferred, for the carbonic acid set free when a strong acid is added to a carbonate interferes to some extent with the indications of alkalinity, acidity, or neutrality afforded by litmus. The alkali most convenient for use is soda, a solution of which has probably already been made the subject of experiment in operations with the standard solution of oxalic acid. It should be kept in a stoppered bottle and exposed to air as little as possible.

VOLUMETRIC SOLUTION OF SODA.

(Hydrate of Sodium, $NaHO = 40$.)

This aqueous solution of soda is most conveniently made of such a strength that each 1000 c.c. contains one molecular weight in grammes of the alkali ($NaHO = 40$). It will be seen from the following equation that 40 grammes of soda convert 63 grammes of oxalic acid into neutral oxalate of sodium. Therefore, 1 litre of this solution, containing 40 grammes of soda, will form a neutral solution of oxalate with 1 litre of standard oxalic acid solution, or with a chemically equivalent quantity of oxalic acid solution of any other strength.

$$\underbrace{H_2C_2O_4,2H_2O}_{\substack{2)\underline{126}\\ 63 = 1000\text{ c.c. of stand. sol.}}} + \underbrace{2NaHO}_{\substack{2)\underline{80}\\ 40 = 1000\text{ c.c. of standard solution.}}} = Na_2C_2O_4 + 4H_2O$$

If pure soda were at hand, it would only be necessary to weigh 40 grammes, dissolve this in water, and dilute to 1 litre. But pure soda cannot readily be produced. Therefore weigh about 45 grammes of hydrate of sodium of trade, and add water to 1 litre. When dissolved take, say, 14 c.c., dilute with more water in a flask, add a few drops of tincture of litmus, and titrate with oxalic acid solution of known strength. Suppose that the volume of standard acid solution required to neutralize the 14 c.c. of soda solution the strength of which is to be estimated has been 15 c.c., or an equivalent amount of acid solution of another strength; then, how many c.c. of soda solution is equivalent to 1000 c.c. of standard acid solution? or, what comes to the same thing, how many c.c. of soda solution contain 40 grammes of real soda ($NaHO$)? As 15 c.c. standard acid are to 14 c.c. soda solution, so are 1000 c.c. standard acid to x c.c. $x = 933$ c.c. 933 c.c. of the soda solution contain, therefore, 40 grammes of soda. This may either be diluted, every 933 c.c. to 1000 c.c., so that it may be standard (1000 c.c. = 40 grammes $NaHO$), or the solution may be used without dilution (933 c.c. = 40 grammes $NaHO$). It has already been mentioned that soda nearly always contains carbonate. To remove resulting carbonic acid, therefore, gentle heat should be employed toward the close of each titration in all the estimations with this solution. Litmus is used throughout as an indicator of completion of the reaction. The following substances are officially estimated with this solution. The list admits of considerable extension (see Sutton's *Volumetric Analysis*).

Acetic Acid.—Operate upon about 1 gramme of glacial acid, about 20 grammes of dilute acid, or about 3 grammes of ordinary acetic acid.

$$\underbrace{HC_2H_3O_2}_{60} + \underbrace{NaHO}_{40 = 1000 \text{ c.c. standard solution.}} = NaC_2H_3O_2 + H_2O$$

Acetic Acid, U. S. P., should contain 36 per cent of real acid ($HC_2H_3O_2$); Dilute Acetic Acid, U. S. P., 6 per cent; Glacial Acetic Acid, U. S. P., 99 per cent.

Citric Acid.—Operate on about 1 gramme. The reaction is expressed by the following equation, etc.:—

$$\underbrace{H_3C_6H_5O_7,H_2O}_{\substack{3)\underline{210}\\ 70}} + \underbrace{3NaHO}_{\substack{3)\underline{120}\\ 40 = 1000 \text{ c.c. standard solution.}}} = Na_3C_6H_5O_7 + 4H_2O$$

Citric Acid, U. S. P., should be pure (= 100 per cent. $H_3C_6H_5O_7,H_2O$).

Hydrochloric Acid.—Operate on from 1 to 2 grammes of the concentrated acid or on about 4 grammes of the dilute acid.

$$\underbrace{HCl}_{36.4} + \underbrace{NaHO}_{40 = 1000 \text{ c.c. standard solution.}} = NaCl + H_2O$$

Hydrochloric Acid, U. S. P., should contain 31.9 per cent. of real acid (HCl), and Dilute Hydrochloric Acid, U. S. P., 10 per cent.

Dilute Hydrobromic Acid.—Operate on from 8 to 12 c.c.

$$\underbrace{HBr}_{80.8} + \underbrace{NaHO}_{40 = 1000 \text{ c.c. standard solution.}} = NaBr + H_2O$$

Dilute Hydrobromic Acid, U. S. P., should contain 10 per cent. of real acid (HBr).

Lactic Acid.—Operate on 1.5 to 2 grammes. The reaction is expressed by the following equation:—

$$\underbrace{HC_3H_5O_3}_{90} + \underbrace{NaHO}_{40 = 1000 \text{ c.c. of standard solution.}} = NaC_3H_5O_3 + H_2O$$

Lactic Acid, U. S. P., should represent 75 per cent. of absolute lactic acid ($HC_3H_5O_3$).

Nitric Acid.—Operate on from 1 to 2 grammes of concentrated or on from 4 to 5 grammes of dilute acid.

$$\underbrace{HNO_3}_{63} + \underbrace{NaHO}_{40\ =\ \text{grammes in 1000 c.c. standard solution.}} = NaNO_3 + H_2O$$

Nitric Acid, U. S. P., should contain 69.4 per cent., and Dilute Nitric Acid, U. S. P., 10 per cent., of real acid (HNO_3).

Sulphuric Acid.—Operate upon from .5 to 1 gramme of concentrated acid or from 4 to 5 grammes of either Dilute or Aromatic Sulphuric Acid.

$$\underbrace{H_2SO_4}_{\substack{2)\underline{98}\\ 49}} + \underbrace{2NaHO}_{\substack{2)\underline{80}\\ 40\ =\ \text{grammes in 1000 c.c. standard solution.}}} = Na_2SO_4 + 2H_2O$$

Sulphuric Acid, U. S. P., should contain not less than 96 per cent., Dilute, U. S. P., 10 per cent. of real acid, and Aromatic, U. S. P., 18 per cent., of sulphuric acid (H_2SO_4), partly as ethyl-sulphuric acid.

Tartaric Acid.—Operate upon about 1 gramme of the acid. The following equation, etc. represents the reaction:—

$$\underbrace{H_2C_4H_4O_6}_{\substack{2)\underline{150}\\ 75}} + \underbrace{2NaHO}_{\substack{2)\underline{80}\\ 40\ =\ \text{grammes in 1000 c.c. standard solution.}}} = Na_2C_4H_4O_6 + 2H_2O$$

Tartaric Acid, U. S. P., should contain 100 per cent. of $H_2C_4H_4O_6$.

Notes.—1. Pure acetates, citrates, tartrates, and some other organic salts have an alkaline action on litmus, but not to an important extent. If the soda solution be added to acetic, citric, or tartaric acid containing litmus until the liquid is fairly blue, the operator will obtain trustworthy results. In delicate experiments turmeric, "methyl-orange," "phenolphthalein," etc. may be used instead of litmus.

2. The operations for the quantitative analysis or measurement of acids are often collectively spoken of under the name of *acidimetry*.

QUESTIONS AND EXERCISES.

995. Calculate the percentage of real acid present in diluted sulphuric acid, 30 grammes of which are neutralized by 84 c.c. of the official volumetric solution of soda. *Ans.* 13.72.

996. Show how much real nitric acid is contained in a solution 36 grammes of which are saturated by 94 c.c. of the standard solution of soda. *Ans.* 16.45 per cent.

ESTIMATION OF ACIDULOUS RADICALS PRECIPITATED BY NITRATE OF SILVER.

The purity of many salts and the strength of their solutions may be determined by this process. Diluted Hydrocyanic Acid, Bromide of Potassium, Bromide of Ammonium, Cyanide of Potassium, Bromide of Sodium, Syrup of Hydriodic Acid, Syrup of Bromide of Iron, and Syrup of Iodide of Iron are quantitatively analyzed by standard solution of nitrate of silver.

STANDARD SOLUTION OF NITRATE OF SILVER.

(Nitrate of Silver, $AgNO_3 = 169.7$.)

Dissolve 16.97 grammes of crystals of pure nitrate of silver in 1 litre of water. 1000 c.c. of this solution contain $\frac{1}{10}$ of the molecular weight in grammes of nitrate of silver. It is therefore a decinormal solution.

Pure crystals of nitrate of silver can readily be obtained. When this is not the case, and pure chloride of sodium is at hand, a solution may be made of approximate strength, and then be standardized by means of that salt. The method may be thus indicated:—

$$\underbrace{NaCl}_{\substack{10)\underline{58.5}\\5.85}} + \underbrace{AgNO_3}_{\substack{10)\underline{169.7}\\16.97}} = AgCl + NaNO_3$$

16.97 = grammes in 1000 c.c. of standard solution.

Take rather less than 1 gramme of the chloride of sodium (NaCl) and dissolve in water. The salt (AgCl) precipitated in the reaction is an insoluble salt, and the end of its precipitation will serve as a good indication of the completion of the reaction. A better indicator, however, is a few drops of neutral chromate of potassium (which should previously be purified by recrystallization). The nitrate of silver does not act upon the chromate until·all the chloride is converted into chloride of silver, after which a deep-red precipitate of chromate of silver is produced. This indication is extremely delicate, and in practice is noticed when the white color due to chloride of silver changes to yellowish from formation of the first traces of chromate of silver. The titration being accomplished, suppose that .1 gramme of the chloride of sodium has taken 17 c.c. of the nitrate of silver solution of unknown strength: how many c.c. of the solution are equivalent to 5.85 of the chloride of sodium? that is, how many c.c. of solution contain 16.97 grammes of nitrate of silver? As .1 gramme of NaCl is to 17 c.c., so are 5.85 NaCl to x c.c. = 994 c.c. 994 c.c. of the solution of nitrate of silver are equivalent, therefore, to 1000 c.c. of official standard solution, and contain 16.97 grammes of the nitrate of silver. They may be diluted to 1000 c.c. if desired.

Hydrocyanic Acid.—Three to four grammes of the dilute acid form a convenient quantity to operate upon. The HCN is first converted into KCN or NaCN with potash or soda. The following equations, etc. explain the reactions:—

$$\underbrace{2HCN}_{\substack{10)54\\5.4}} + 2NaHO = \underbrace{2NaCN}_{\substack{10)98\\9.8}} + 2H_2O$$

$$\underbrace{2NaCN}_{\substack{10)98\\9.8}} + \underbrace{AgNO_3}_{\substack{10)169.7\\16.97\ =\ \text{grammes in 1000 c.c. of standard solution.}}} = AgCN,NaCN + NaNO_3$$

It is seen that 5.4 grammes of real hydrocyanic acid (HCy) are equivalent to 9.8 grammes of cyanide of sodium, and represent 16.97 grammes of nitrate of silver, or 1000 c.c. of standard solution of nitrate of silver.

The cyanide of sodium having been obtained, the titration is carried on until it is converted into the soluble double salt (NaCy,AgCy), immediately after which a permanent turbidity occurs, due to precipitation of cyanide of silver, thus:—

$$AgCy,NaCy + AgNO_3 = 2AgCy + NaNO_3.$$

This turbidity affords a delicate and satisfactory proof of the completion of the above reaction, which is the B. P. process.

There is, however, a difficulty in the conversion of the acid into the cyanide (Siebold) to which it is necessary to pay particular attention. Tincture of litmus is added to the acid diluted largely with water, and the soda poured in. Owing to the strong alkaline reaction of the cyanide of sodium formed, the mixture becomes blue when only a small proportion of the acid has been converted. If then the titration be conducted until the turbidity appears, only the cyanide of sodium will be estimated, leaving free hydrocyanic acid still unacted upon. Indeed, cyanide of sodium may be estimated in presence of hydrocyanic acid in this way. Thus the following reaction (expressed approximately) might occur:

$$\underbrace{NaCy + 4HCy}_{\text{Alkaline.}} + AgNO_3 = \underbrace{AgCy + NaNO_3 + 4HCy}_{\text{Turbid and acid.}}$$

In this case only one-fifth of the acid originally present would be estimated. The mixture would, however, become acid. If this acidity be prevented all difficulty is overcome. The following details (Senier) will be found to answer well: To the diluted hydrocyanic acid add soda solution to a strong alkaline reaction, determined by means of tincture of litmus. Then add the silver solution, drop by drop, from the burette, when in most cases the mixture will become acid. When it does so, add more soda solution, and repeat this process until the final reading, when the solution must be alkaline. In this way the addition of too much soda at the commencement, which would use up silver solution and make the reading a trifle too high, is avoided.

Dilute Hydrocyanic Acid, U. S. P., should contain 2 per cent. of real acid (HCN), as shown by the following process:—

The following is the quantitative test of purity ordered by the United States Pharmacopœia:—" 13.5 gm. diluted with 30 c.c. of water, and mixed with enough of an aqueous suspension of magnesia to make the mixture quite opaque, and afterward with a few drops of solution of chromate of potassium, should require 50 c.c. of the volumetric solution of nitrate of silver before the red color caused by the latter ceases to disappear on stirring (corresponding to the presence of 2 per cent. of absolute Hydrocyanic Acid)." By this method the whole of the HCy is precipitated as AgCy before the chromate of silver is permanently precipitated, and 13.5 grammes of dilute HCy, U. S. P., will therefore require 100 c.c. of volumetric nitrate of silver, not 50 c.c., as stated by the Pharmacopœia.

Bromide of Ammonium.—Operate upon .075 to .1 gramme of the salt, using chromate of potassium (or Bichromate, U. S. P.) as an indicator of the close of the reaction:—

$$\underbrace{NH_4Br}_{\substack{10)\underline{97.8}\\ 9.78}} + \underbrace{AgNO_3}_{\substack{10)\underline{169.7}\\ 16.97\ =\ \text{1000 c.c. of standard solution.}}} = AgBr + NH_4NO_3.$$

Bromide of Ammonium, U. S. P., should be of 97 per cent. purity, but as the impurity is chloride of ammonium, this too will be precipitated by the nitrate of silver, and must be calculated in finding the percentage of bromide.

$$\underbrace{NH_4Cl}_{\substack{10)\underline{53.5}\\ 5.35}} + \underbrace{AgNO_3}_{\substack{10)\underline{169.7}\\ 16.97\ =\ \text{1000 c.c. of standard solution.}}} = AgCl + NH_4NO_3.$$

The amount of the salt equivalent to 1000 c.c. of standard solution is first calculated by simple proportion: Let x represent this; then $9.78 - x = y$, the excess of standard solution used up by the chloride of ammonium, reckoned in terms of bromide (NH_4Br); and since 5.35 grammes of $NH_4Cl = 9.78$ grammes of NH_4Br, the excess which ammonium chloride can consume is represented by $9.78 - 5.35 = 4.43$;

therefore, as $4.43 : 5.35 :: y : z =$ the amount of chloride of ammonium present in x grammes of the sample taken; lastly, the percentage is calculated by simple proportion:

As $x : 100 :: z : p =$ percentage. For example: .075 gramme of the salt required, 7.8 c.c. of standard solution,

1. $7.8 : 1000 :: .075 : x;$
   $x = 9.615.$
2. $9.78 - 9.615 = y;$
   $y = .165.$
3. $4.43 : 5.35 :: .165 : z;$
   $z = .19926.$
4. $9.615 : 100 :: .19926 : p;$
   $p = 2.072$ per cent. of NH_4Cl.

Bromide of Potassium.—Operate upon rather less than .1 gramme, and conduct the titration in the same manner as with chloride of sodium, using chromate of potassium as an indicator of the close of the reaction:—

$$\underbrace{\text{KBr}}_{\substack{10)\underline{118.8}\\ 11.88}} + \underbrace{\text{AgNO}_3}_{\substack{10)\underline{169.7}\\ 16.97 \text{ = grammes in 1000 c.c. of standard solution.}}} = \text{AgBr} + \text{KNO}_3$$

To calculate the KCl, proceed as for NH_4Cl, 74.5 of KCl being equal to 118.8 of KBr.

The United States Pharmacopœia requires Bromide of Potassium to contain 97 per cent. of the salt.

Bromide of Sodium.—Operate upon .1 gramme, and proceed exactly as for bromide of ammonium:—

$$\underbrace{\text{NaBr}}_{\substack{10)\underline{102.8}\\ 10.28}} + \underbrace{\text{AgNO}_3}_{\substack{10)\underline{169.7}\\ 16.97 \text{ = 1000 c.c. of standard solution.}}} = \text{AgBr} + \text{NaNO}_3$$

Bromide of Sodium, U. S. P., should be of 97 per cent. purity, and the chloride may be calculated in the same manner as chloride of ammonium, 5.85 grammes of chloride being equal to 10.28 grammes of bromide of sodium.

Cyanide of Potassium.—Operate upon from .1 to .2 gramme of the salt, conducting the titration as for hydrocyanic acid. The following reaction occurs:—

$$\underbrace{\text{2KCy}}_{\substack{10)\underline{130}\\ 13}} + \underbrace{\text{AgNO}_3}_{\substack{10)\underline{169.7}\\ 16.97 \text{ = 1000 c.c. of standard solution.}}} = \text{AgCy,KCy} + \text{KNO}_3$$

The United States Pharmacopœia requires Cyanide of Potassium to contain 90 per cent. of real cyanide (KCy).

Syrup of Hydriodic Acid.—Operate upon 10 to 15 grammes. The reaction which occurs is as follows:—

$$\underbrace{\text{HI}}_{\substack{10)\underline{127.6}\\ 12.76}} + \underbrace{\text{AgNO}_3}_{\substack{10)\underline{169.7}\\ 16.97 \text{ = 1000 c.c. of standard solution.}}} = \text{AgI} + \text{HNO}_3$$

The close of the reaction is shown by the cessation of the formation of iodide of silver, the nitric acid liberated rendering chromate of potassium inadmissible as an indicator.

Syrupus Acidi Hydriodici, U. S. P., should contain 1 per cent. of anhydrous hydriodic acid (HI).

Syrup of Bromide of Iron.—About 1 gramme should be used:—

$$\underbrace{\text{FeBr}_2}_{\substack{20)\underline{215.5}\\ 10.775}} + \underbrace{\text{2AgNO}_3}_{\substack{20)\underline{339.4}\\ 16.97 \text{ = 1000 c.c. of standard solution.}}} = \text{2AgBr} + \text{Fe}(\text{NO}_3)_2$$

It should correspond to 10 per cent. of bromide of iron ($FeBr_2$) to fulfil the requirements of the United States Pharmacopœia.

Syrup of Iodide of Iron.—Operate upon 1 to 2 grammes of the syrup until no further precipitate is formed:—

$$\underbrace{FeI_2}_{\substack{20)309.1 \\ 15.455}} + \underbrace{2AgNO_3}_{\substack{20)339.4 \\ 16.97}} = 2AgI + Fe(NO_3)_2$$

16.97 = 1000 c.c. of standard solution.

Syrupus Ferri Iodidi, U. S. P., should contain 10 per cent. of iodide of iron (FeI_2).

Spirit of Wine (*Spiritus Rectificatus*, B. P.) may contain traces of amylic alcohol and aldehyd; these may be detected by nitrate of silver, which is reduced by them to the metallic state. Any quantity beyond a mere trace of such bodies renders spirit of wine too impure for use in medicine. "Four fluidounces with thirty grain-measures (about 2 c.c.) of the volumetric solution of nitrate of silver exposed for twenty-four hours to bright light, and then decanted from the black powder which has formed, undergoes no further change when again exposed to light with more of the test."—B. P. "If 20 c.c. are shaken in a glass-stoppered vial, previously well rinsed with the same alcohol, with 2 c.c. of test-solution of nitrate of silver, the mixture should not be rendered more than faintly opalescent during one day's exposure to direct sunlight (abs. of more than traces of foreign organic matters, fusel oil, etc.)."—U. S. P.

Iodide of Potassium may be volumetrically estimated by a semidecinormal solution of mercuric chloride, the termination of the operation being indicated by the formation of a red precipitate:—

$$(1)\ 4KI + HgCl_2 = 2KCl + \underset{\text{(soluble)}}{HgI_2,2KI};$$

$$(2)\ HgI_2,2KI + HgCl_2 = 2KCl + 2HgI_2.$$

The author of this process, M. Personne, states that neither chlorides, bromides, nor carbonates interfere. Carles dissolves the iodide in spirit of wine of 17½ per cent., as much excess of water decomposes the double iodide.

Iodide of Iron.—Messrs. Naylor and Hooper have demonstrated that Personne's solution is applicable to ferrous iodide, even in the state of syrup:—

$$(1)\ 2FeI_2 + HgCl_2 = FeCl_2 + \underset{\text{(soluble)}}{FeI_2,HgI_2};$$

$$(2)\ FeI_2,HgI_2 + HgCl_2 = FeCl_2 + 2HgI_2.$$

QUESTIONS AND EXERCISES.

997. Explain the volumetric method of estimating the strength of aqueous solutions of hydrocyanic acid.

998. Work a sum showing how much nitrate of silver will indicate, by the official volumetric process, the presence of 1 part of real hydrocyanic acid. *Ans.* 6.2853 parts.

ESTIMATION OF SUBSTANCES READILY OXIDIZED.

Any deoxidizer—that is, any substance which quickly absorbs a definite amount of oxygen or is susceptible of any equivalent action—may be quantitatively tested by ascertaining how much of an oxidizing agent of known power must be added to a given quantity before complete oxidation is effected. The oxidizing agents employed for this purpose in the United States Pharmacopœia are iodine and the red chromate of potassium. Permanganate of potassium is often used for the same purpose. Iodine acts indirectly by taking hydrogen from water and liberating oxygen; the red chromate of potassium directly, by the facility with which it yields three-sevenths of its oxygen, as indicated by the equations and statements given on p. 575; permanganate of potassium, by affording five-eighths of its oxygen in presence of acid,

$$2K_2Mn_2O_8 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2.$$

Standard Solution of Iodine.

(Iodine, I = 126.6.)

If pure iodine be not at hand, it may be prepared by mixing the commercial article with about a fourth of its weight of iodide of potassium and subliming. Sublimation may be effected by gently warming the mixture in a beaker the mouth of which is closed by a funnel; the iodine vapor condenses on the funnel, while fixed impurities are left behind, and any chlorine which the iodine may contain is absorbed by the iodide of potassium, an equivalent quantity of iodine being liberated. Small quantities may be similarly treated between two watch-glasses placed edge to edge. Any trace of moisture in the resublimed iodine is removed by exposure for a few hours under a glass shade near a vessel containing oil of vitriol.

Place 12.66 grammes of pure iodine and about 18 grammes of pure iodide of potassium (an aqueous solution of which is the best solvent of iodine; the salt plays no other part in these operations) in a litre flask, add a small quantity of water, and agitate until the iodine is dissolved; dilute to 1 litre.

The following substances are officially estimated by this volumetric solution:—

Sulphurous Acid.—Operate on about .5 of a gramme of the acid, and dilute with water as usual. If the sulphurous acid be diluted to a less degree than .04 or .05 per cent., there will be some risk of the sulphuric acid formed being again reduced to sulphurous acid, with liberation of iodine. In delicate experiments the distilled water used for dilution should previously be freed from air by boiling, to prevent the small amount of oxidizing action which dissolved air would exert. The solution of iodine is then added until a slight permanent brown tint is produced, showing the presence of free iodine. A better indicator of the termination of the reaction is mucilage of starch, which gives a blue color with the slightest trace of free iodine.

The following equations, etc. show the reaction that takes place:—

$$\underbrace{H_2SO_3} + H_2O + \underbrace{I_2} = 2HI + H_2SO_4$$

20)82 20)253.2

4.1 12.66 = grms. in 1000 c.c. of standard solution.

$$H_2O,\underbrace{SO_2} + H_2O + \underbrace{I_2} = 2HI + H_2SO_4$$

20)64 20)253.2

3.2 12.66 = grms. in 1000 c.c. of standard solution.

The official (U. S. P.) sulphurous acid should contain 3.5 per cent. of sulphurous anhydride (SO_2).

Arsenic.—About .1 gramme of *solid arsenic*, accurately weighed, should be dissolved in the usual quantity of water, heated to boiling, by help of about .5 gramme of bicarbonate of sodium. The arsenious acid is only partly, if at all, converted into arsenite or arseniate of sodium, but the iodine reaction occurs more readily in an alkaline solution. When the liquid is quite cold, mucilage of starch is added, and the iodine solution allowed to flow in until, after well stirring, a permanent blue color is produced. The official *solution of arsenite of potassium*, already containing some carbonate of potassium, requires somewhat less. 10 grammes is a convenient quantity to operate upon. To this should be added the usual quantity of water and about .3 of a gramme of bicarbonate of sodium. After boiling and cooling the titration is carried on as before.—About 10 grammes of the official *solution of arsenic in dilute hydrochloric acid* is also a convenient quantity to operate upon. This quantity requires about .6 gramme of bicarbonate of sodium. The usual quantity of water is added, and the titration performed as before. The following equation exhibits the reaction:—

$$\underbrace{As_2O_3} + 5H_2O + \underbrace{2I_2} = 4HI + 2H_3AsO_4$$

40)197.8 40)506.4

4.945 12.66 = grms. in 1000 c.c. of standard solution.

Arsenic, U. S. P., should contain 97 per cent., and both solutions, U. S. P., contain .97 per cent. of arsenic.

Hyposulphite of Sodium.—About .4 of a gramme is a convenient quantity to employ. It is dissolved in water, starch mucilage added, and the iodine solution slowly run in, the whole being frequently stirred, until a permanent blue color is produced. This is the B. P. process; the U. S. P. orders a solution of sodium hyposulphite to be shaken with solid iodine.

In the previous reactions iodine has acted as an indirect oxidizing agent by uniting with the hydrogen and thus liberating the oxygen of water. In the present case it unites with an analogue of hydrogen—namely, sodium—a new salt (tetrathionate of sodium) being simultaneously produced, thus:—

$$\underbrace{2(Na_2S_2O_3,5H_2O)} + \underbrace{I_2} = 2NaI + Na_2S_4O_6 + 10H_2O$$

20)496 20)253.2

24.8 12.66 = grms. in 1000 c.c. of standard solution.

The United States Pharmacopœia requires 98 per cent. purity in the case of hyposulphite of sodium.

Sulphite of Potassium.—About .1 gramme is a convenient quantity to take, using starch paste as an indicator, as before. The reaction as below occurs:—

$$\underbrace{K_2SO_3,2H_2O} + \underbrace{I_2} = 2KI + H_2SO_4 + H_2O$$

2.0)19.4 20)253.2

9.7 12.66 = 1000 c.c. of standard solution.

Sulphite of potassium, U. S. P., should contain 90 per cent. of the crystallized salt ($K_2SO_3,2H_2O$).

Bisulphite of Sodium.—Operate upon .05 to .07 gramme, as before:—

$$\underbrace{NaHSO_3} + \underbrace{I_2} + H_2O = NaI + H_2SO_4 + HI$$

20)104 20)253.2

5.2 12.66 = 1000 c.c. of standard solution.

The United States Pharmacopœia requires bisulphite of sodium to contain 90 per cent. of the pure salt ($NaHSO_3$).

Sulphite of Sodium.—Use for this estimation about 1. to .15 gramme, and proceed as before:—

$$\underbrace{Na_2SO_3,7H_2O} + \underbrace{I_2} = 2NaI + H_2SO_4 + 6H_2O$$

20)252 20)253.2

12.6 12.66 = 1000 c.c. of standard solution.

This also should contain 90 per cent. of the crystallized salt to satisfy the demands of the United States Pharmacopæia.

QUESTIONS AND EXERCISES.

999. Give equations illustrative of the reactions on which the use of a standard volumetric solution of iodine is based.

1000. From what point of view may iodine be regarded as an oxidizing agent?

1001. What reagent indicates the termination of the reaction between deoxidizing substances and moist iodine?

1002. How much sulphurous acid gas will cause the absorption of 2.54 parts of iodine in the volumetric reaction? *Ans.* .642.

1003. What quantity of iodine will be required, under appropriate conditions, to oxidize 5 parts of arsenic? *Ans.* 12.008.

1004. Find by calculation the amount of hyposulphite of sodium and of sulphite of sodium which will react with 13 parts of iodine in volumetric analysis. *Ans.* 25.466 and 12.9384.

VOLUMETRIC SOLUTION OF RED CHROMATE OF POTASSIUM.

(Red Chromate of Potassium, $K_2Cr_2O_7 = 294.8$.)

One molecule of red chromate of potassium in presence of an acid, under favorable circumstances, yields 4 atoms of oxygen to the hydrogen of the acid, leaving three available either for direct oxidation or for combination with the hydrogen of more acid, an equivalent proportion of acidulous radical being liberated for any required purpose.

When used as a volumetric agent the red chromate always yields the whole of its oxygen to the hydrogen of the accompanying acid, a corresponding quantity of acidulous radicals being set free—four-sevenths of this radical immediately combining with the potassium and chromium of the red chromate, three-sevenths becoming available. Ferrous may thus be converted into ferric salts with sufficient rapidity and exactitude to admit of the estimation of an unknown quantity of iron by a known quantity of the red chromate. As 1 atom of any liberated bivalent acidulous radical will convert 2 molecules of ferrous into 1 of ferric salt, 1 molecule of red chromate causes 6 of ferrous to become 3 of ferric, as shown in the following equation:—

$$K_2CrO_4,CrO_3 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4,Cr_23SO_4 + 7H_2O + 3(Fe_23SO_4).$$

The volumetric solution is made by dissolving 14.74 grammes ($\frac{1}{20}$ of a molecular weight in grammes) of red chromate of potassium in water, and diluting to 1 litre. It is used in determining the strength of the ferrous preparations. It is known that the whole of the ferrous has been converted to ferric salt when a small drop of the liquid placed in contact with a drop of a very dilute solution of ferridcyanide of potassium on a white plate ceases to strike a blue color.

If the red chromate employed in making this standard solution is not known to be pure and dry, the strength of the solution may be checked by dissolving a small, accurately weighed piece of pianoforte wire (0.4 or 0.5 gramme) in diluted sulphuric acid in a small flask, warming, and then running in the solution of red chromate until conversion is effected.

The reactions which take place may be thus expressed:—

$$\underbrace{6Fe}_{\substack{20)\underline{335.4}\\16.77}} + 6H_2SO_4 = \underbrace{6FeSO_4}_{\substack{20)\underline{911.4}\\45.57}} + 6H_2$$

$$\underbrace{6FeSO_4}_{\substack{20)\underline{911.4}\\45.57}} + \underbrace{K_2Cr_2O_7}_{\substack{20)\underline{294.8}\\14.74\text{ — grammes in 1000 c.c. of standard solution.}}} + 7H_2SO_4 =$$

$$K_2SO_4,Cr_23SO_4 + 7H_2O + 3(Fe_23SO_4)$$

It is evident that 16.77 grammes of iron are equivalent in the reactions to 14.74 of red chromate or 1000 c.c. of standard solution of the chromate. Now suppose that 0.5 of a gramme of pianoforte wire has been employed, and the quantity of solution of red chromate of unknown strength used has been 28 c.c. How many c.c. of this solution contain 14.74 of red chromate? that is, how many c.c. must be required to oxidize ferrous salt containing 16.77 of iron? As .5 of iron is to 28 c.c. sol., so are 16.77 of iron to x c.c. sol. = 939.12 c.c. Of the supposed solution, then, 939.12 c.c. would contain 14.74 grammes of red chromate, and would be equivalent to 1000 c.c. of standard solution. It might be employed without being diluted, or, better, be diluted to official standard strength.

Special care should be taken in all these estimations of substances readily oxidized to avoid atmospheric oxidation. Flasks may usually be loosely corked, or corked closely with a gas exit-tube passing just beneath a little mercury, and in all cases the estimation should be performed quickly. When standardizing with iron wire any slight oxidation may be remedied by a fragment of zinc, the last portions of which must be removed or dissolved before the titration is commenced.

The ferrous salt in the following substances is estimated by this solution.

Arseniate of Iron.—Operate upon 1 to 2 grammes. Dissolve in excess of dilute sulphuric or hydrochloric acid. Sulphuric acid is preferable in most cases, because ferrous sulphate absorbs oxygen much less readily than ferrous chloride. The reaction that occurs is shown in the following equation, the ferrous arseniate being converted into ferric arseniate:—

$$\underbrace{2(\mathrm{Fe}''_3 2\mathrm{AsO}_4)}_{\substack{20)\underline{891}\\ 44.55}} + 7\mathrm{H}_2\mathrm{SO}_4 + \underbrace{\mathrm{K}_2\mathrm{Cr}_2\mathrm{O}_7}_{\substack{20)\underline{294.8}\\ 14.74 = \text{grammes in 1000 c.c. of standard sol.}}} =$$

$$\mathrm{K}_2\mathrm{SO}_4,\mathrm{Cr}_2 3\mathrm{SO}_4 + \mathrm{Fe}'''_2 3\mathrm{SO}_4 + 2(\mathrm{Fe}'''_2 2\mathrm{AsO}_4) + 7\mathrm{H}_2\mathrm{O}$$

Arseniate of Iron, B. P., is supposed to contain 37.9 per cent. of ferrous arseniate. The compound is more nearly a ferric than a ferrous arseniate.

Phosphate of Iron.—Operate upon 1 to 2 grammes. Proceed as with arseniate. The following equation indicates the reaction, the ferrous phosphate being converted into ferric phosphate:—

$$\underbrace{2(\mathrm{Fe}''_3 2\mathrm{PO}_4)}_{\substack{20)\underline{715.4}\\ 35.77}} + 7\mathrm{H}_2\mathrm{SO}_4 + \underbrace{\mathrm{K}_2\mathrm{Cr}_2\mathrm{O}_7}_{\substack{20)\underline{294.8}\\ 14.74 = \text{1000 c.c. of standard solution.}}} =$$

$$\mathrm{K}_2\mathrm{SO}_4,\mathrm{Cr}_2 3\mathrm{SO}_4 + \mathrm{Fe}'''_2 3\mathrm{SO}_4 + 2(\mathrm{Fe}'''_2 2\mathrm{PO}_4) + 7\mathrm{H}_2\mathrm{O}$$

The official (B. P.) requirement is nearly 45 per cent. of real ferrous phosphate. Phosphate of Iron, U. S. P., is *Ferric Phosphate*, and therefore cannot be estimated by this solution.

Saccharated Carbonate.—Proceed as with arseniate, using about the same quantity:—

$$\underbrace{6FeCO_3} + 13H_2SO_4 + \underbrace{K_2Cr_2O_7} =$$

20)695.4 20)294.8

34.77 14.74 = 1000 c.c. of standard solution.

$$K_2SO_4Cr_23SO_4 + 3(Fe_23SO_4) + 13H_2O + 6CO_2$$

The official (U. S. P.) strength is 15 per cent. Trade samples yield from 20 to 30, and sometimes 35, per cent., according to the care with which oxidation has been prevented. The theoretical percentage obtainable from the ingredients is 45.5, the quantity that would be present if the compounds were anhydrous and unoxidized—conditions never obtained in practice. Howie has suggested that as hydrochloric acid is known to so rapidly convert ordinary sugar into inverted sugar as to render it easily attacked by chromic acid, while phosphoric acid very slowly affects sugar, the latter acid instead of the former should be employed in dissolving the saccharated carbonate of iron for volumetric analysis. Another mode of eliminating the action of sugar is to char with oil of vitriol before analyzing.

Magnetic Oxide of Iron.—Use about the same quantity, and proceed as with arseniate or phosphate. The reaction may thus be shown:—

$$\underbrace{6Fe_3O_4} + 31H_2SO_4 + \underbrace{K_2Cr_2O_7} =$$

20)1390.2 20)294.8

69.51 14.74 = grammes in 1000 c.c. of standard solution.

$$K_2SO_4,Cr_23SO_4 + 9(Fe_23SO_4) + 31H_2O$$

or,

$$6(Fe_2O_3,\underbrace{FeO}) + 31H_2SO_4 + \underbrace{K_2Cr_2O_7} =$$

20)431.4 20)294.8

21.57 14.74 = grammes in 1000 c.c. of stand. solution.

$$K_2SO_4,Cr_23SO_4 + 9(Fe_23SO_4) + 31H_2O$$

Absolutely pure magnetic oxide of iron contains 31 per cent. of ferrous oxide. Oxidation occurs, however, during manufacture, as in the case of the ferrous salts just described. The British Pharmacopœia recognizes magnetic oxide containing nearly 25 per cent. of ferrous oxide.

Sulphate of Iron.—Operate upon about 1 gramme of the crystallized or precipitated salt in presence of excess of sulphuric acid; the reaction which occurs has been already given when treating of the standardizing of solution of Bichromate of Potassium on page 575.

The United States Pharmacopœia demands almost absolute purity for both *Ferri Sulphas* and *Ferri Sulphas Precipitatus* ($FeSO_4,7H_2O$).

Note.—The use of this volumetric solution in quantitative analysis admits of great extension. The student should at least employ it in the case of a few iron ores.

QUESTIONS AND EXERCISES.

1005. Write equations explanatory of the oxidizing power of red chromate of potassium.

1006. One hundred cubic centimetres of an aqueous solution of red chromate of potassium contain $\frac{1}{200}$ of the molecular weight of the salt in grammes; with what weight of metallic iron, dissolved in hydrochloric acid, will this volume react? *Ans.* 1.677 grammes.

1007. If 8.34 grammes of impure crystallized ferrous sulphate, dissolved in acidulated water, require 93 c.c. of the standard solution of chromate for complete conversion into ferric salt, what percentage of ferrous sulphate is present? *Ans.* 92.966.

1008. Work a sum showing how much red chromate of potassium is required for the conversion of 10 parts of ferrous sulphate into ferric salt. *Ans.* 1.768.

1009. Show what quantity of pure ferrous carbonate is indicated by 1.475 parts of red chromate as applied in volumetric analysis. *Ans.* 3.479.

1010. Prove what amount of official saccharated carbonate of iron is equivalent to .7375 part of red chromate in the volumetric reaction. *Ans.* 11.598.

ESTIMATION OF SUBSTANCES READILY DEOXIDIZED.

Any substance which quickly yields a definite amount of oxygen may be quantitatively tested by ascertaining how much of a deoxidizing agent of known power must be added to a given quantity before complete deoxidation is effected. The chief compounds which may be used for this absorption of oxygen (deoxidizers or reducing agents, as they are commonly termed) are hyposulphite of sodium, sulphurous acid, ferrous sulphate,* oxalic acid, arsenious acid. The first named is officially employed; it is only used in the estimation of free iodine, and, indirectly, of chlorine and chlorinated compounds. Iodine and chlorine are regarded as oxidizing agents, because their great affinity for hydrogen enables them to become powerful indirect oxidizers in presence of water.

STANDARD SOLUTION OF HYPOSULPHITE OF SODIUM.

(Crystallized Hyposulphite of Sodium, $Na_2S_2O_3,5H_2O = 248$.)

Dissolve about 27 grammes of hyposulphite of sodium in a litre or less of water. Fill a burette with this solution, and allow it to flow into a beaker containing, say, 15 c.c. of the volumetric solution of iodine until the brown color of the iodine is just discharged, or, starch being added, until the blue iodide of starch is decolorized. (The latter affords the more delicate indication.) When iodine and hyposulphite of sodium react, 2 atoms of iodine remove 2 of sodium from 2 molecules of the hyposulphite, tetrathionate of sodium being formed, as indicated in the following equation:—

---

* Five grains of permanganate of potassium dissolved in water require for decoloration a solution of forty-four grains of granulated sulphate of iron acidulated with two fluidrachms of diluted sulphuric acid.

$$\underbrace{I_2}_{\substack{20)253.2\\ 12.66 = \text{grms. of iodine in 1000 c.c.}}} + \underbrace{2(Na_2S_2O_3,5H_2O)}_{\substack{20)496\\ 24.8 = \text{grms. of hypo. in 1000 c.c.}}} =$$

$$2NaI + Na_2S_4O_6 + 10H_2O$$

Now, suppose the number of c.c. required to deoxidize the 15 c.c. of standard iodine were 14 c.c., how many c.c. of this hyposulphite solution would be equivalent to 1000 c.c. of standard iodine solution? In other words, how many c.c. would contain 24.8 grammes of hyposulphite? As 15 c.c. iodine sol. are to 14 c.c. hyposulph. sol., so are 1000 iodine sol. to x hyposulph. sol. = 933 c.c. Therefore, 933 c.c. of this solution of hyposulphite would contain 24.8 grammes of the salt, and be equivalent to 1000 c.c. of the official standard solution. The 933 c.c. would be diluted to 1000 c.c., or be used without dilution. In either case its strength would, as usual, be recorded on the label. The following substances are estimated officially by means of this solution.

Chlorine-Water.—About 10 grammes are operated upon. Excess of iodide of potassium is added; that is, to 10 grammes of solution of chlorine about half a gramme of iodide. An amount of iodine is set free by the chlorine exactly in proportion to their atomic weights. The titration is then conducted as already described. The following shows the reaction:—

$$\underbrace{Cl_2}_{\substack{20)71\\ 3.55}} + 2KI = \underbrace{I_2}_{\substack{20)253.2\\ 12.66}} + 2KCl$$

$$\underbrace{I_2}_{\substack{20)253.2\\ 12.66}} + \underbrace{2(Na_2S_2O_3,5H_2O)}_{\substack{20)496\\ 24.8 = \text{grammes in 1000 c.c. of standard solution.}}} = 2NaI + Na_2S_4O_6 + 10H_2O$$

It is evident, then, that 1000 c.c. of standard solution of hyposulphite of sodium, or a corresponding quantity of a solution of different strength, is equivalent to 3.55 grammes of chlorine gas. Chlorine-Water of the United States Pharmacopœia contains .4 per cent. of chlorine gas.

Iodine.—Solid iodine is dissolved in solution of iodide of potassium, and titrated as already described. About .2 of a gramme is a convenient quantity to employ. 1000 c.c. of standard hyposulphite solution are equivalent, as seen in the equation, to 12.66 of iodine. The United States Pharmacopœia requires "iodine" to contain 100 per cent. of real iodine. It is assumed in this operation that the iodine has been shown by qualitative analysis to be free from chlorine and bromine. These elements resemble iodine in reacting upon hyposulphite of sodium, hence would reckon as iodine in a volumetric assay.

Chlorinated Lime.—Operate on from .1 to .2 of a gramme. Dissolve in the usual quantity of water, and add excess either of dilute hydrochloric or dilute sulphuric acid and of iodide of potassium: .1 to .2 of a gramme of chlorinated lime would require .4 to .8 of a gramme of iodide of potassium. The following equations show the reactions:—

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2;$$

or,

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The chlorine thus set free liberates an equivalent amount of iodine, and this is titrated as before. (See the equations for solution of chlorine.) This chlorine, liberated from chlorinated lime by acids, is its available chlorine for indirect oxidizing action. It should correspond (U. S. P.) to 25 per cent.

Solution of Chlorinated Lime.—About 2 grammes is a convenient quantity to operate upon. 1 gramme of iodide of potassium and excess of acid should be added, and the available chlorine determined as in the case of the solid. The official (U. S. P.) requirement is 2.9 per cent. of available chlorine.

Solution of Chlorinated Soda.—About 2 grammes are mixed with the usual quantity of water, excess of acid added, and about 1 gramme of iodide of potassium. The available chlorine is estimated as in the case of chlorinated lime. The reaction by which the chlorine is evolved is similar:—

$$NaCl,NaOCl + 2HCl = 2NaCl + H_2O + Cl_2.$$

The action of the liberated chlorine on the iodide of potassium and the iodine on the hyposulphite solution has been given under "Solution of Chlorine." The official (U. S. P.) requirement is 2 per cent. of available chlorine.

Compound Solution of Iodine.—Process as before, using 1 or 2 grammes; the reaction has already been given. The requirements of the United States Pharmacopœia are 5 per cent. of free iodine.

Tincture of Iodine.—Use about 1 gramme. It will contain 8 per cent. of free iodine when of official strength.

QUESTIONS AND EXERCISES.

1015. For what purposes is the official volumetric solution of hyposulphite of sodium used?

1016. On what reaction is based the quantitative employment of hyposulphite of sodium?

1017. How much hyposulphite of sodium is required to show the presence of 10 parts of iodine? *Ans.* 19.527.

1018. To what amount of chlorine is 4.96 parts of hyposulphite of sodium equivalent in volumetric analysis? *Ans.* 0.71.

1019. Describe the operation included in the estimation of the strength of bleaching-powder.

1020. By what reagent is the complete absorption of free iodine by hyposulphite of sodium indicated?

MISCELLANEOUS PROBLEMS.

1021. Work sums showing how much bicarbonate of potassium is contained in an eight-ounce bottle of medicine, seven fluidrachms of which are saturated by two and a half grains of crystallized oxalic acid. *Ans.* 36.3 grains.

1022. A sample of soda-ash is said to contain 78 per cent. of pure anhydrous carbonate of sodium; if the statement is true, how much of the official volumetric solution of oxalic acid will saturate 5 grammes of the specimen? *Ans.* 73.6.

1023. 2.69 grammes of common brown sulphuric acid are saturated by 43.5 cubic centimetres of the official volumetric solution of soda; how much acid of 96.8 per cent. is present? *Ans.* The 2.69 contained 2.2.

1024. Four grammes of a litre and a half of concentrated hydrocyanic acid are neutralized by 89 cubic centimetres of volumetric solution of nitrate of silver of official strength by the official process: to what volume must the bulk of the acid be diluted for the production of acid of pharmacopœial strength? *Ans.* 4½ litres.

1025, 3.18 grammes of a powder containing arsenic require for complete reaction 84 cubic centimetres of a volumetric solution of iodine, which is 1.43 per cent. weaker than the standard solution of the United States Pharmacopœia; what percentage of pure arsenic is contained in the powder? *Ans.* 12.863.

1026. How much pure metal is present in a sample of iron 1.68 of a gramme of which, dissolved in dilute sulphuric acid, is exactly attacked by 95.7 cubic centimetres of semi-decinormal volumetric solution of red chromate of potassium which is 6 per cent. too strong?

GRAVIMETRIC QUANTITATIVE ANALYSIS.

ESTIMATION OF METALS.

POTASSIUM.

Outline of the Process.—This element is usually estimated in the form of double chloride of potassium and platinum. Qualitative analysis having proved the presence of potassium and other radicals in a substance, a small quantity of the material is accurately weighed, dissolved, and the other elements removed by appropriate reagents; the precipitates are well washed, in order that no trace of the potassium salt shall be lost, the resulting liquid concentrated over a water-bath (to avoid loss that would occur mechanically during ebullition), hydrocholoric acid added if necessary, solution of perchloride of platinum poured in, and evaporation continued to dryness; excess of the perchloride is then dissolved out by adding to the dried residue spirit of wine containing half its bulk of ether (a liquid in which the double chloride is insoluble), the mixture carefully poured on to a tared and dried filter, washed with the spirit till every trace of free perchloride of platinum is removed, the whole dried and weighed; from the resulting amount the proportion of potassium, or equivalent quantity of a salt of potassium, is ascertained by calculation.

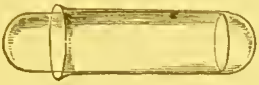
Note.—From this short description it will be seen, first, that the chemistry of quantitative is the same as that of qualitative analysis; second, that the principle of gravimetric is the same as that of volumetric quantitative analysis: the combining proportions being known, unknown quantities of elements may be ascertained by calculation from known quantities of their compounds.

Apparatus.—In addition to a delicate balance and weights and the common utensils, a few special instruments are used in quantitative manipulation; some of these may be prepared before proceeding with the estimation of potassium.

Filtering-paper may be of the kind known as "Swedish," the texture of which is of the requsite degree of closeness and its ash small in amount. A large number of circular pieces of one size, six to eight centimetres in diameter, should be cut ready for use. In delicate experiments, where a precipitate on a filter has to be ignited and the paper consequently burnt, the weight of the ash of the filter must be deducted from the weight of the residue. The ash is estimated after burning ten or twenty of the cut filters. These are folded into a small compass, a portion of a piece of platinum wire twisted a few times round the packet, so as to form a cage, the whole held by the free end of the wire over a weighed porcelain crucible placed in the centre of a sheet of glazed paper, the bundle ignited by a spirit-lamp or smokeless gas-flame, the flame allowed to impinge against the charred mass till it falls into the crucible below, any stray fragments on the sheet carefully shaken into the crucible, the latter placed over a flame till carbon has all burnt off and nothing but ash remains, the whole cooled, weighed, and the weight of the crucible deducted; the weight of the residue divided by the number of pieces used gives the average amount of ash in each filter.

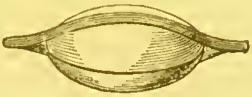
A pair of weighing-tubes (Fig. 74), for holding dried filters during operations at the balance, may be made from two test-tubes, one fitting closely within the other. About five centimetres of the closed end of the outer and seven of the inner are cut off by leading a crack round the tube with a

Fig. 74.



A pair of weighing-tubes.

Fig. 75.



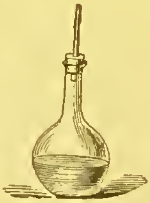
Clamped watch-glass for weighing.

pencil of incandescent charcoal, and the sharp edges fused in the blowpipe-flame. A filter, after drying, is quickly folded and placed in the narrower tube, the mouth of which is then closed by the wider tube. This prevents reabsorption of moisture from the air.

A pair of watch-glasses, having accurately ground edges and clamped, as shown in Fig. 75, also form a convenient arrangement for weighing filters, etc.

The washing-bottle, holding the *spirit of wine and ether*, is a common flask through the cork of which a short straight tube passes. The outer end of the tube should be sufficiently narrowed to enable it to deliver a very fine stream of the liquid. The flask being inverted, the warmth of the hand expands the air and vapor to a sufficient extent to force out the liquid.

Fig. 76.



The washing-bottle.

The ordinary washing-bottle for quantitative operations should be formed of a flask in which water may be boiled, fitted up as usual (*vide* p. 107).

A water-oven is the best form of drying-apparatus. It is a small square copper vessel, jacketed on five sides and having a door on the sixth; water is poured into the space between the inner and outer casing, and the whole placed over a gas-lamp or source of heat, moist air and steam escaping by appropriate apertures. Desiccation at higher temperatures than the boiling-point of water may be practised by using oil or paraffin instead of water, inserting a thermometer in the fat. The apparatus may be purchased of any maker of chemical instruments.

Pure distilled water must be used in all quantitative determinations.

Note.—In practising the operations of quantitative analysis, experiments should at first be conducted on definite salts of known composition, for the accuracy of results may then be tested by calculation.

Estimation of Potassium in the Form of Double Chloride of

Potassium and Platinum.—Select two or three crystals of pure nitrate of potassium, powder them in a clean mortar, dry the powder by gently heating in a porcelain crucible over a flame for a few seconds, place about a couple of decigrammes (0.2 grm.) of the powder in a counterpoised watch-glass, accurately weigh the selected quantity, transfer to a small dish, letting water from a wash-bottle flow over the watch-glass and run into the dish, warm the dish till the nitrate is dissolved, acidulate with hydrochloric acid, add excess of aqueous solution of perchloride of platinum (a quantity containing about 0.4 of solid salt), evaporate to dryness over a water-bath. While evaporation is going on place a filter and the weighing-tubes in the water-oven, exposing them to a temperature of 100° C. for about half an hour; fold the filter and insert it in the tubes, place them on a plate under a glass shade, and when cold accurately note their weight. Arrange the weighed filter in a funnel over a beaker. Transfer the dried and cooled platinum salt from the dish to the filter by moistening the residue with the mixture of alcohol and ether, and when the salt is loosened pouring the contents of the dish into the paper cone. Any salt still adhering may be freed by the finger, which, together with the dish, should be washed in the stream of spirit, the rinsings at once flowing into the filter. The filtrate should have a yellowish-brown color, due to the excess of perchloride of platinum. If it is colorless, an insufficient amount of perchloride has been added, and the whole operation must be repeated. The washed precipitate and filter are finally dried in the water-oven, folded and placed in the weighing-tubes, the drying continued until the whole, after repeated weighing when cold, ceases to alter; the final weight is noted.

Note.—If filters are not freed from all trace of acid by thorough washing, the paper will be brittle when dry, falling to pieces on being folded.

Analytical memoranda in the note-book may have the following form:—

Watch-glass and substance . . . . .
Watch-glass . . . . ________
Substance . . . . ________
Weighing tubes, filter, and Pt salt . . .
Weighing tubes and filter . . . . ________
$PtCl_4,2KCl$ . . . ________

The calculations are simple:—

$$\text{As}\left\{\begin{matrix}\mathrm{PtCl_4,2KCl}\\ =484.8\end{matrix}\right\}\text{ are equivalent to }\left\{\begin{matrix}\mathrm{2KNO_3}\\ =202\end{matrix}\right\},$$

$$\text{so}\left\{\begin{matrix}\text{the weight of}\\ \text{double chloride}\\ \text{obtained}\end{matrix}\right\}\text{ is equivalent to } x.$$

x will be the amount of *pure* nitrate of potassium in the quantity of substance operated on. x should, in the present instance, be identical with the weight of substance taken, because, for educational purposes, pure nitre is under examination. Only after analyses of pure substances have yielded the operator results identical with those by calculation can analyses of substances of unknown degree of purity be undertaken with confidence. A Table of Atomic Weights, from which to find molecular weights, is given in the Appendix.

Platinum residues should be preserved, and the metal recovered from them from time to time (*vide* p. 245).

Hot alcohol sometimes reduces perchloride of platinum, the metal being thrown out of solution in a finely-divided form known as *platinum black;* only aqueous solutions, therefore, of the salt should be used where heat is employed. Hence, also, in washing out excess of perchloride of platinum from the double chloride of platinum and potassium by spirit the application of heat should be avoided.

Effervescing Potash-water (*Liquor Potassæ Effervescens*, B. P.) is most easily estimated volumetrically (p. 561). Any adulteration by an equivalent amount of bicarbonate of sodium would, however, by that process be undetected; hence the Pharmacopœia directs that "5 fluidounces, evaporated to one-fifth, and 12 grains of tartaric acid added, yield a crystalline precipitate which, when dried, weighs not less than 12 grains." Five fluidounces of this preparation should contain 7.5 grains of bicarbonate, convertible into 14.1 grains of acid tartrate of potassium by 11.25 grains of tartaric acid. The method is somewhat rough, but quite efficient for "potash-water" containing nothing but bicarbonates of alkali-metals.

Proportional Weights of Equivalent Quantities of Potassium and its Salts.

Metal	K_2	78
Oxide ("potash")	K_2O	94
Hydrate ("caustic potash")	2KHO	112
Carbonate (anhydrous) . .	K_2CO_3	138
Carbonate (crystalline) . .	K_2CO_3 + 16 % aq. .	164.285
Bicarbonate	$2KHCO_3$	200
Nitrate	$2KNO_3$	202
Platinum salt	$PtCl_4,2KCl$ . . .	484.8

SODIUM.

Sodium is usually estimated as sulphate. Accurately weigh a porcelain crucible and lid, place within about .3 grm. of pure rock-salt, and again weigh, making a memorandum of the weights in a note-book. Add rather more strong sulphuric acid than may be considered sufficient to convert the chloride into acid sulphate of sodium. Heat the crucible gradually, the flame being first directed against the side of the crucible to avoid violent ebullition, until fumes of acid cease to be evolved, toward the end of the operation dropping in one or two fragments of carbonate of ammonium to facilitate complete expulsion of all excess of acid. When cold, weigh the crucible and contents. The weight of the crucible having been deducted, the amount of sulphate obtained should be the exact equivalent of the quantity of chloride of sodium employed.

$$\underbrace{2NaCl}_{117} + H_2SO_4 = \underbrace{Na_2SO_4}_{142} + 2HCl.$$

Proportional Weights of Equivalent Quantities of Sodium and its Salts.

Metal	Na_2	46
Oxide ("soda")	Na_2O	62
Hydrate ("caustic soda")	$2NaHO$	80
Carbonate (anhydrous)	Na_2CO_3	106
Carbonate (crystals)	$Na_2CO_3,10H_2O$	286
Bicarbonate	$2NaHCO_3$	168
Chloride	$2NaCl$	116.8
Sulphate (anhydrous)	Na_2SO_4	142
Sulphate (crystals)	$Na_2SO_4,10H_2O$	322

AMMONIUM.

Salts of ammonium are, for purposes of quantitative analysis, generally converted into the double chloride of ammonium and platinum ($PtCl_4,2NH_4Cl$), the details of manipulation being the same as those observed in the case of potassium. About 0.15 grm. of pure, white, dry chloride of ammonium may be taken for experiment.

COMPOSITION OF THE PLATINUM SALT.

		In 1 molec. wt.	In 100 parts.
Pt	194.4	194.4	43.903
Cl_6	35.4 × 6	212.4	47.967
N_2	14.0 × 2	28	6.324
H_8	1.0 × 8	8	1.806
		442.8	100.000

			In 1 molec. wt.	In 100 parts.
or,	$PtCl_4$	336	336	75.88
	$2NH_4Cl$	53.4 × 2	106.8	24.12
			442.8	100.00

The proportion of nitrogen, ammonium, or chloride of ammonium in the double chloride may also be ascertained from the weight of platinum left on igniting the double chloride; for this purpose heat must be applied slowly, or platinum will be mechanically carried off with the gaseous products of decomposition.

Proportional Weights of Equivalent Quantities of Ammoniacal Compounds.

Ammonia (gas)	$2NH_3$	34
Ammonium	$(NH_4)_2$?	36
Chloride of ammonium	$2NH_4Cl$	106.8
Platinum salt	$PtCl_4,2NH_4Cl$	442.8
"Carbonate of ammonium"	$(N_4H_{16}C_3O_8) \div 2$	118
Sulphate of ammonium	$(NH_4)_2SO_4$	132

BARIUM.

Barium is estimated in the form of anhydrous sulphate of barium ($BaSO_4$).

Process.—Dissolve 0.3 or 0.4 grm. of pure crystallized and dried chloride or nitrate of barium in about half a litre of water in a beaker, heating to incipient ebullition, and slightly acidulating with hydrochloric or nitric acid. Add diluted sulphuric acid (prepared some days previously, so that sulphate of lead may have deposited) so long as a precipitate forms; keep the mixture hot for some time, set aside for half an hour, pass the supernatant liquid through a filter, gently boil the residue two or three times with more water; finally, collect the precipitate on the filter, removing adherent particles from the beaker by the finger and cleansing by a stream of hot water from the wash-bottle. The precipitate must be washed with hot water until the filtrate ceases to turn litmus-paper red or give any cloudiness when tested with chloride of barium. The filter and sulphate of barium, having thoroughly drained, are dried in a warm place, commonly by supporting the funnel in an inverted bottomless beaker over a sand-bath or hot plate.

The sulphate of barium is now removed from the filter, heated to drive off every trace of moisture, and weighed. This is accomplished by placing a weighed porcelain crucible (and cover) on a sheet of glazed paper, holding the filter over it, and carefully transferring the precipitate; the sides of the filter are then gently rubbed together and detached powder dropped into the crucible, the paper folded, encased in two or three coils of one end of a platinum wire and burnt over the crucible, ash and any particles in the sheet of paper dropped into the sulphate of barium, the open crucible exposed over a flame till its contents are quite white, covered, cooled, and weighed.

	Formulæ.	Molecular weights.
Chloride of barium	$BaCl_2,2H_2O$.	243.6
Nitrate of barium	$Ba2NO_3$.	260.8
Sulphate of barium . . .	$BaSO_4$.	232.8

Composition of Sulphate of Barium.

		In 1 molec. wt.	In 100 parts.
Ba	136.8	136.8 .	58.77
S	32	32 . .	13.73
O_4	16×4 . . .	64 . .	27.50
		232.8	100.00

In these educational experiments it is unnecessary to take filter-ash into account. Inevitable mistakes of manipulation commonly cause far greater errors.

CALCIUM.

Calcium is usually thrown out of solution in the form of oxalate, the precipitate ignited, and the resulting carbonate weighed.

Process.—Dissolve 0.3 grm. or 0.4 of dried colorless crystals of calc-spar in about a third of a litre of water acidulated with hydrochloric acid, heat the solution to near the boiling-point, add excess of solution of oxalate of ammonium, then ammonia, until, after stirring, the liquid smells strongly ammoniacal; set aside in a warm place for twelve hours. Carefully pour off the supernatant liquid, passing it through a filter; add hot water to the precipitate, set aside for half an hour, again decant, and after once more washing transfer the precipitate to the filter, allowing all contained fluid to pass through before a fresh portion is added. Wash the precipitate with hot water, avoiding a rapid stream or the precipitate may be driven through the pores of the paper. Dry, transfer to a weighed crucible, and incinerate, as described for sulphate of barium, and slowly heat the precipitate till the bottom of the crucible is just visibly red when seen in the dark. As soon as the residue is white or only faintly gray remove the lamp, cool, and weigh.

The resulting carbonate of calcium should have the same weight as the calc-spar from which it was obtained. If loss has occurred, carbonic acid gas has probably escaped. In that case moisten the residue with water, and after a few minutes test the liquid with red litmus- or turmeric-paper; if an alkaline reaction is noticed, it is due to the presence of caustic lime. Add a small lump of carbonate of ammonium, evaporate to dryness over a water-bath, and again ignite, this time being careful not to go beyond the prescribed temperature. The treatment may, if necessary be repeated.

Proportional Weights of Equivalent Quantities of Calcium Salts.

Oxide (quicklime)	CaO	56
Hydrate (slaked lime)	$Ca2HO$	74
Carbonate	$CaCO_3$	100
Sulphate (anhydrous)	$CaSO_4$	136
Sulphate (crystalline or precipitated)	$CaSO_4,2H_2O$	172
Chloride	$CaCl_2$	111
Phosphate (of bone)	$(Ca_3 2PO_4)310 \div 3$	103.3
Superphosphate	$CaH_4 2PO_4$	234

MAGNESIUM.

Process 1.—The light or heavy carbonate of magnesium of pharmacy may be estimated by heating a weighed quantity to redness in a porcelain crucible. If it has the composition indicated by the formula given in the British Pharmacopœia ($3MgCO_3.Mg2HO,4H_2O$), it will yield 42 per cent. of magnesia (MgO). According to that work, the purity of even sulphate of magnesium ($MgSO_4,7H_2O$) may be determined by boiling a weighed quantity with excess of carbonate of sodium, collecting the precipitate, washing, drying, igniting, and weighing the resulting magnesia (MgO). The crystalline sulphate should afford 16.26 per cent. of oxide. The official solution of carbonate of magnesium in carbonic acid water (*Liquor Magnesiæ Carbonatis*, B. P.) should yield five grains of pure oxide of magnesium per fluidounce.

Process 2.—The general form in which magnesium is precipitated is as phosphate of ammonium and magnesium ($MgNH_4PO_4,6H_2O$); this, by heat, is converted into pyrophosphate of magnesium ($Mg_2P_2O_7$). Accurately weigh a small quantity (0.4 to 0.5 grm.) of pure dry crystals of sulphate of magnesium, dissolve in two or three hundred cubic centimetres of cold water in a beaker, add chloride of ammonium, ammonia, and phosphate of sodium or ammonium, agitate with a glass rod (without touching the sides of the vessel, or crystals will firmly adhere to the rubbed portions), and set aside for twelve hours. Collect on a filter, wash the precipitate with water containing a tenth of its volume of the strongest solution of ammonia, until the filtrate ceases to give a precipitate with an acidulated solution of nitrate of silver. Dry, transfer to a crucible, burn the filter in the usual way, heat slowly to redness, cool, and weigh.

Proportional Weights of Equivalent Quantities of Magnesium Salts.

Pyrophosphate . .	$Mg_2P_2O_7$	222
Sulphate	$2(MgSO_4,7H_2O)$	492
Oxide	$2(MgO)$	80
Official carbonate .	$(3MgCO_3,Mg2HO,4H_2O) \div 2$ . .	191

ZINC.

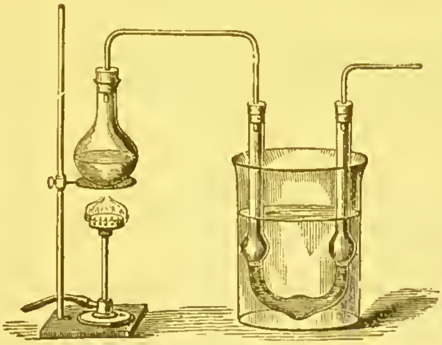
Zinc is usually estimated as oxide (ZnO), occasionally as sulphide (ZnS).

Process.—Dissolve a weighed quantity (0.5 to 0.6 grm.) of sulphate of zinc in about half a litre of water in a beaker, heat to near the boiling-point, add carbonate of sodium in slight excess, boil, set aside for a short time; pass the supernatant liquid through a filter, gently boil the precipitate with more water, again decant; repeat these operations two or three times; collect the precipitate on the filter, wash, dry, transfer to a crucible, incinerate, ignite, cool, and weigh. 286.9 (= molec. weight) of sulphate should yield 80.9 (= molec. weight) of oxide.

MANGANESE.

To ascertain its value for evolving chlorine from hydrochloric acid a weighed quantity of finely-powdered black oxide of manganese is heated in a small flask with pure hydrochloric acid, and the resulting chlorine conveyed into a U-tube containing solution of iodide of potassium. The amount of iodine thus freed is estimated by the volumetric solution of hyposulphite of sodium. 126.6 of iodine indicate 35.4 of chlorine. Manganese may also be estimated by the reaction and apparatus described under "Oxalates," page 607. (See Fig. 77).

Fig. 77.



ALUMINIUM.

Aluminium is always precipitated as hydrate (Al_26HO) and weighed as oxide (Al_2O_3).

Process.—Dissolve about 2 grammes of pure dry ammonium alum in half a litre of water, heat the solution, add chloride of ammonium and a slight excess of ammonia, boil gently till the odor of ammonia has nearly disappeared, set aside for the hydrate to deposit, pass the supernatant liquid through a filter, wash the precipitate three or four times by decantation, transfer to the filter, finish the washing, dry, burn the filter, ignite in a covered crucible, and weigh.

$Al_23SO_4K_2SO_4,24H_2O$	948
$Al_23SO_4,(NH_4)_2SO_4,24H_2O$	907
Al_2O_3	103
Per cent. of Al_2O_3 yielded by ammonium alum	11.356

QUESTIONS AND EXERCISES.

1027. Give details of the manipulations observed in gravimetrically estimating salts of potassium or ammonium.

1028. What quantity of chloride of sodium is contained in a sample of rock-salt 0.351 gramme of which yields 0.426 of sulphate of sodium? *Ans.* 99.83 per cent.

1029. To what amount of the official alum is 0.894 of a gramme of the double chloride of platinum and potassium equivalent? *Ans.* 1.748 grammes.

1030. Find the weight of sulphate of barium obtainable from 0.522 of nitrate. *Ans.* 0.466.

1031. Describe the usual method by which salts of calcium are estimated.

1032. By what quantitative processes may the official salts of magnesium be analyzed?

1033. Calculate the proportion of pure sulphate of zinc in a sample of crystals 0.574 of which yield 0.161 of oxide. *Ans.* 99.46 per cent.

1034. Ascertain the weight of alumina (Al_2O_3) which should be obtained from 1.814 grammes of ammonium alum.

IRON.

Iron and its salt are gravimetrically estimated in the form of ferric oxide (Fe_2O_3).

Compounds containing organic acidulous radicals are simply incinerated, and the resulting oxide weighed. Thus, 1 gramme of the official citrate of iron and ammonium (*Ferri et Ammoniæ Citras*, B. P.), incinerated, with exposure to air, leaves not less than .27 of ferric oxide. A small quantity of the salt is weighed in a tared covered porcelain crucible, flame cautiously applied until vapors cease to be evolved, the lid then removed, the crucible slightly inclined and exposed to a red heat until all carbonaceous matter has disappeared. The residual ferric oxide is then weighed. The tartrate of potassium and iron (*Ferrum Tartaratum*, B. P.) is treated in the same manner, except that the ash must be washed and again heated before weighing, in order to remove carbonate of potassium produced during incineration: 5 grammes should yield 1.5 grammes of ferric oxide.

From other compounds of iron, soluble in water or acid, the metal is precipitated in the form of hydrate (Fe_26HO) by solution of ammonia, and converted into oxide (Fe_26O_3) by ignition. Dissolve a piece (about 0.2 grm.) of the purest iron obtainable (piano wire), accurately weighed, in water acidulated with hydrochloric acid; add a few drops of nitric acid and gently boil; pour in excess of ammonia, stir, set aside till the ferric hydrate has deposited, pass the supernatant liquid through a filter, treat the precipitate three or four times with boiling water; transfer to the filter, wash till the filtrate yields no trace of chlorine (for chloride of ammonium will decompose ignited ferric oxide, with volatilization of ferric chloride), dry and ignite as usual, and weigh. Iron in the official solutions (*Liquor Ferri Perchloridi Fortior*, *Liquor Ferri Nitratis*, and *Liquor Ferri Tersulphatis*) may be estimated by this general process.

The proportion of metallic iron in a mixture of iron and oxides of iron may be determined by digestion in a strong solution of iodine in iodide of potassium, which attacks the metal only. The reduced iron of pharmacy (*Ferrum Reductum*) is in good condition so long as it contains, as shown by this method, half its weight of free metal.

Another Method.—Reduced iron is converted into ferrous chloride by a hot, strong solution of corrosive sublimate, while the oxides are not affected. The filtrate may be treated gravimetrically or volumetrically (Wilner).

Proportional Weights of Equivalent Quantities of Iron and its Salts.

Metal	Fe_2	111.8
Ferric oxide	Fe_2O_3	159.8
Ferric hydrate	Fe_26HO	213.8
Ferric chloride	Fe_2Cl_6	324.2
Ferric sulphate	Fe_23SO_4	399.8
Ferrous sulphate	$2(FeSO_4,7H_2O)$	555.8

ARSENICUM.

Arsenic (As_2O_3) is usually estimated volumetrically (*vide* p. 573). With certain precautions arsenicum may also be precipitated and weighed as sulphide (As_2S_3).

Process 1.—The pure, white, massive arsenic (about 0.2 grm.) is dissolved in a flask in a small quantity of water containing bicarbonate of sodium or potassium, the liquid being heated. A slight excess of hydrochloric acid is then added, and surphuretted hydrogen gas passed through the solution so long as a precipitate falls, the mouth of the flask being stopped by a plug of cotton-wool (to prevent undue access of air and consequent decomposition of the gas, resulting in precipitation of sulphur). The mixture is warmed in the flask, and carbonic acid gas passed through it until the odor of sulphuretted hydrogen has nearly disappeared; the precipitate collected on a tared filter, washed as quickly as possible with hot water containing a little sulphuretted hydrogen, dried in a water-oven, and weighed. 197.8 parts of arsenic should yield 245.8 of sulphide of arsenicum.

Process 2.—The arsenicum must be present in the arsen*ic* condition. If the operator is not certain that this is the case, the solution must be warmed with a little hydrochloric acid and a few grains of chlorate of potassium added until a distinct odor of chlorous vapor is evolved, which is then allowed to escape by continued application of heat. To the solution thus obtained ammonia, which must produce no turbidity, is added in excess, and then magnesia mixture (see p. 608). The solution is set aside for twenty-four or forty-eight hours. The precipitate is collected on a filter and washed with as little ammonia-water (1 to 3) as possible until the filtrate ceases to give a reaction for chlorides. The precipitate is then dried on the filter, the precipitate and filter-paper burned, and the whole gently ignited in a crucible and weighed. The residue is represented by the formula ($Mg_2As_2O_7$).

ANTIMONY.

The metal is precipitated in the form of sulphide (Sb_2S_3), with the precautions observed in estimating arsenicum, a small quantity of tartaric acid, as well as hydrochloric, being added to prevent the precipitation of an oxysalt. If the sulphuretted hydrogen be passed through a hot solution, the particles of precipitate aggregate better, and the latter may be more quickly filtered out and washed. Tha experiment may be performed on about half a gramme of pure tartar-emetic: the salt should yield slightly more than half its weight (50.6 per cent.) of sulphide. According to Fresenius, the sulphide dried at 100° C. still contains 2 per cent. of water, and must be heated in a current of carbonic acid gas until it turns from an orange to a black color before all moisture is expelled. In the United States Pharmacopœia the purity of tartar-emetic (*Antimonium Tartaratum*) and the strength of solution of chloride of antimony (*Liquor Antimonii Chloridi*) are determined by the above process. *Sulphurated Antimony* of official quality, when dissolved in hydrochloric acid and the solution boiled and poured into a considerable volume of water. should yield a precipitate of oxychloride, which, after washing and drying, should weigh 85 per cent. of the sulphurated antimony.

COPPER.

Copper is precipitated from its solutions and weighed (1) as metal (Cu_2) or (2) as oxide (CuO).

Process 1.—Dissolve about half a gramme of dry crystallized sulphate of copper in a small quantity of water in a tared porcelain crucible or beaker, acidulate with hydrochloric acid, introduce a fragment or two of pure zinc, cover the vessel with a watch-glass, and set aside till evolution of hydrogen has ceased and the still acid liquid is colorless. The copper is then washed with hot water by decantation until no trace of acid remains, the precipitate drained, rinsed with strong spirit of wine, dried in the water-oven, and weighed.

Process 2.—About three-fourths of a gramme of sulphate of copper is accurately weighed, dissolved in half a litre of water, the liquid boiled; dilute solution of potash or soda is then added till no more precipitate falls, ebullition continued for a short time, and the beaker set aside; the supernatant liquid is decanted, the precipitate boiled with water, twice or thrice collected on a filter, washed, dried, transferred to a crucible, the filter incinerated, and its ash moistened with a drop of nitric acid; the whole is finally heated strongly, cooled, and weighed.

Process 3.—From a solution acidulated by sulphuric acid and placed in a platinum crucible copper may be entirely deposited in a coherent form by a weak current of electricity, the crucible being connected with the zinc pole of the battery, a platinum spatula suspended in the solution forming the positive pole. The crucible may afterward be freed from the deposited copper by nitric acid.

249.2 parts of sulphate of copper yield 79.2 of oxide or 63·2 of metal.

Other Processes.—*Vide Pharmaceutical Journal* for April 3, 1880, p. 801.

BISMUTH.

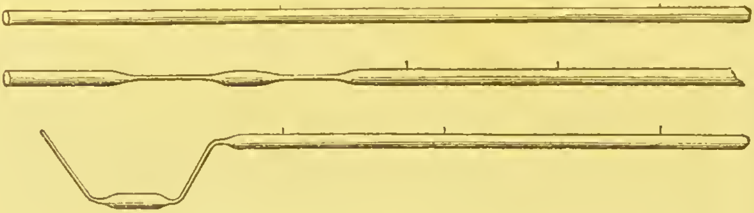
Dissolve 0.3 or 0.4 grm. of pure oxycarbonate of bismuth ($2Bi_2O_2CO_3,H_2O$) (*Bismuthi Subcarbonas*, U. S. P.) in a small quantity of hydrochloric acid, dilute with water slightly acidulated by hydrochloric acid, pass excess of sulphuretted hydrogen through the liquid, collect the precipitate on a tared filter, wash, dry at 100° C., and weigh. The sulphide must not be exposed too long in the water-oven, or it will increase in weight, owing to absorption of oxygen; hence it should be tested in the balance every half hour during desiccation. 521 of oxycarbonate should yield 516 of sulphide (Bi_2S_3). The atomic weight of bismuth is 210.

MERCURY.

This element may be (1) isolated and estimated in the form of metal, or precipitated and weighed as (2) mercurous chloride, or (3) mercuric sulphide.

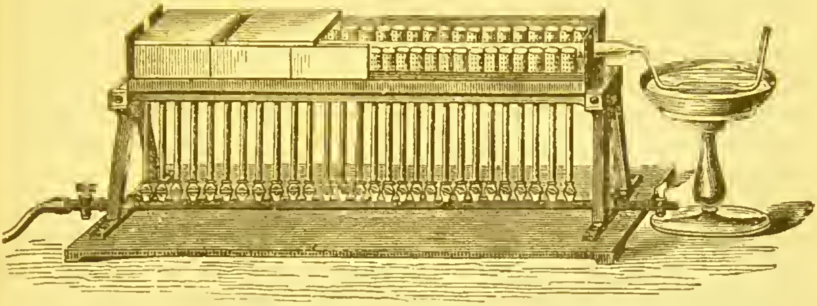
Process 1.—The process by which the metal itself is separated is one of distillation into a bulb surrounded by water. About half a metre of the difficultly fusible German glass known as *combustion-tubing* is sealed at one end after the manner of a test-tube (Fig. 78); a mixture of bicarbonate of sodium and dry chalk is then dropped into the tube to the height of 2 or 3 centimetres, and, next, several small fragments of quicklime so as to occupy another centimetre: a mixture of about a gramme of pure calomel or corrosive sublimate with enough powdered quicklime to occupy 10 or 12 centimetres of the tube is added; then the lime-rinsings of the mixing-mortar, a layer of a few centimetres of powdered quicklime, and finally a plug of *asbestos* (a fibrous mineral unaffected by heat), The whole powder should occupy two-thirds of the length of the tube. The part of the tube just above the asbestos is now softened in the blowpipe-flame and drawn out about a decimetre to the diameter of a narrow quill; it is again drawn out to the same extent at a point about two or three centimetres nearer the mouth, and any excess of tubing cut off. The bulb thus formed may be enlarged by softening and blowing. The tube is next softened at a point close to but anterior to the asbestos, and bent to form an obtuse angle; the tube is then softened close to the bulb and slightly bent, so that the bulb may be parallel with the large tube; then softened on the other side of the bulb, and the terminal tube bent to an obtuse angle, so that, the tube being held in a horizontal position, the bulb may be sunk in water and the terminal tube point upward (Fig. 80). The long tube is now laid in the gas-furnace found in most laboratories (Fig. 81), a basin so placed that the bulb of the apparatus may be cooled by being surrounded by water, the part of the tube occupied by asbestos heated to redness, and the flame slowly lengthened until the whole tube is red hot. Under the circumstances just described the mercurial compound volatilizes, is decomposed by the lime, and its acidulous radical fixed, the mercury carried to and condensed in the bulb, the carbonic acid gas evolved from the bicarbonate of sodium and chalk washing out the last portions of mercury vapor from the tube. When the distillation is considered to be complete, the dish of water is removed, the bulb dried, and then detached by help of a file at a point beyond any sublimate of mercury. The bulb is lastly weighed, the mercury shaken or dissolved out, and the tube again dried and weighed.

Figs. 78, 79, 80.



Process 2.—The process by which mercury is separated in the form of calomel consists in adding hydrochloric and phosphorous acids (*vide* p. 348) to an aqueous or even acid solution of a weighed quantity of the mercurial compound, setting the mixture aside for twelve hours, collecting the precipitate on a tared filter, washing, drying at 100° C., and weighing (Rose). The experiment may be tried on half a gramme to a gramme of corrosive sublimate.

Fig. 81.



Distillation of Mercury for Quantitative Purposes.

Process 3.—Two or three decigrammes of corrosive sublimate are dissolved in water, the solution acidulated with hydrochloric acid, excess of sulphuretted hydrogen passed through it, the precipitate collected on a tared filter, washed with cold water, dried at 100° C., and weighed.

Proportional Weights of Equivalent Quantities of Mercury and its Salts.

Metal	Hg	199.7
Mercurous chloride	$HgCl$	235.1
Mercuric chloride	$HgCl_2$	270.5
Mercuric sulphide	HgS	231.7

LEAD.

Lead is generally estimated either as (1) oxide, (2) sulphate, (3) chromate, or (4) metal.

Process 1.—Weigh out 1 or 2 grammes of pure acetate of lead in a covered crucible previously tared, and heat slowly until no more vapors are evolved. Remove the lid, stir down the carbonaceous mass with a clean iron wire, and keep the crucible in the flame so long as any carbon remains unconsumed. Introduce some fragments of fused nitrate of ammonium, and again ignite until no metallic lead remains and all excess of the nitrate has been decomposed. Cool and weigh the resulting oxide (PbO).

Process 2.—Dissolve 0.4 or 0.5 of a gramme of acetate of lead in a small quantity of water, drop in diluted sulphuric acid, add to the mixture twice its bulk of methylated spirit of wine, and set aside. Decant the supernatant liquid, collect the sulphate on a filter, wash with spirit, dry, transfer to a porcelain crucible, removing as much of the sulphate as possible from the paper, incinerate on the crucible-lid (not in the platinum coil, for the particles of reduced lead would unite with the platinum by fusion), ignite, cool, and weigh.

Process 3.—About half a gramme of acetate of lead is dissolved in 200 or 300 c.c. of water, acetic acid added, and then solution of red chromate of potassium. Collect the precipitate on a tared filter, wash, dry at 100° C., and weigh.

Process 4.—In certain cases, notably in that of commercial white lead, the lead may be estimated in the metallic state by means of cyanide of potassium. The lead paint (about 20 grammes) is weighed and carefully incinerated. The residue, a mixture of metallic lead and oxide of lead, is then mixed with several times its bulk of cyanide of potassium and the whole heated to fusion. With careful manipulation the lead collects in one globule, which, after cooling, may readily be separated from the mixed cyanide and cyanate and weighed. White lead, commercially pure, should contain 74 per cent. of lead.

Molecular Weight of Salts of Lead.

Metal	Pb	206.5
Acetate	$Pb2C_2H_3O_2,2H_2O$	378.5
Oxide	PbO	222.5
Sulphate	$PbSO_4$	302.5
Chromate	$PbCrO_4$	322.9

SILVER.

Compounds of silver which are readily decomposed by heat are estimated in the form of (1) metal, others usually as (2) chloride (AgCl), but sometimes as (3) cyanide (AgNC).

Process 1.—Heat about a gramme of oxide of silver (Ag_2O) in a tared crucible, cool, and weigh. 231.4 of oxide yield 215.4 of metal. "29 grains heated to redness yield 27 grains of metallic silver."—*Brit. Pharm.*

Process 2.—Dissolve 0.4 or 0.5 grm. of pure dry crystals of nitrate of silver in water, acidulate with two or three drops of nitric acid, slowly add hydrochloric acid, stirring rapidly, until no more precipitate falls. Pour off the supernatant liquid through a filter, wash the chloride of silver once or twice with hot water, transfer to the filter, complete the washing, and dry. After removing as much as possible of the precipitate from the paper to the crucible, burn the filter, letting its ash fall on the inverted lid of the crucible, moisten with a drop of nitric acid, warm, add a drop of hydrochloric acid, evaporate to dryness, replace the lid on the crucible, unite the whole until the edges of the mass of chloride begin to fuse; cool and weigh. 169.7 of nitrate yield 143.1 of chloride. According to the United States Pharmacopœia, 10 parts of nitrate should thus yield 8.4 of chloride, while 20 parts of "moulded nitrate of silver" should yield 16 of chloride, and the filtrate from the chloride evaporated to dryness should leave no residue, indicating absence of nitrates of potassium or sodium and other similar adulterants. 20 parts of "diluted nitrate of silver" should yield 8.4 of chloride; 10 parts of "oxide of silver" should yield 12.36 of chloride.

Process 3.—Cyanide of silver may be collected on a tared filter and dried at 100° C. 169.7 of nitrate yield 133.7 of cyanide.

Silver and its salts may be volumetrically estimated by a standard solution of chloride of sodium.

Cupellation.—The amount of silver in an alloy may be also determined by a dry method. The metal is folded in a piece of thin sheet lead, placed on a *cupel* (*cupella*, little cup, made of compressed bone-earth), and heated in a furnace, the cupel being protected from the direct action of flame by a muff-shaped or, rather, oven-shaped, case termed a muffle. The metals melt, the baser become oxidized, the oxide of lead fusing and dissolving the other oxides; the fluid oxides are absorbed by the porous cupel, a button of pure silver remaining. An alloy supposed to contain 95 per cent. of silver requires about three times its weight of lead for successful cupellation; if 92½ per cent. (English silver coin), between five and six times its weight of lead is necessary.

QUESTIONS AND EXERCISES.

1035. Explain the gravimetric process by which the strength of the official solutions of ferric chloride, nitrate, and sulphate is determined.

1036. Mention the various amounts of ferrous and ferric salts equivalent to 100 parts of metal.

1037. State the precautions necessary to be observed in estimating arsenicum or antimony in the form of sulphide.

1038. In what form are the official compounds of bismuth weighed for quantitative purposes?

1039. Give an outline of the process by which mercury may be isolated from its official preparations and weighed in the metallic condition.

1040. Describe three methods for the quantitative analysis of salts of lead, and the weights of the respective precipitates, supposing 0.56 of crystallized acetate to have been operated on in each case.

1041. Describe the process by which silver is estimated in the forms of metal, chloride, and cyanide.

1042. What proportions of nitrate of silver are indicated, respectively, by 15 of metal, 9.8 of chloride, and 8.1 of cyanide?

1043. Describe cupellation.

GRAVIMETRIC ESTIMATION OF THE ACIDULOUS RADICALS OF SALTS.

CHLORIDES.

Free chlorine (chlorine-water) and compounds which by action of acids yield free chlorine (Chlorinated Lime, Chlorinated Soda, and their official solutions) are estimated volumetrically by a standard solution of hyposulphite of sodium (*vide* p. 578). The amount of combined chlorine in pure chlorides (HCl, NaCl) may also be determined by volumetric analysis with a standard solution of nitrate of silver (p. 567).

Combined chlorine is gravimetrically estimated in the form of chloride of silver, the operation being identical with that just described for silver salts (p. 599). 58.4 parts of pure, colorless, crystallized chloride of sodium (rock-salt) yield 143.1 of chloride of silver.

IODIDES.

Free iodine is estimated volumetrically by solutions of hyposulphite of sodium (*vide* p. 579).

Combined iodine is determined gravimetrically in the form of iodide of silver, the operations being conducted as with chloride of silver. Iodide of potassium may be used for an experimental determination: KI = 165.1 should yield AgI = 234.3. Of iodide of cadmium (*Cadmii Iodidum*, B. P.) it is stated that "10 grains dissolved in water, and nitrate of silver added in excess, give a precipitate which, when washed with water and afterward with half an ounce of solution of ammonia, and dried, weighs 12.5 grains."

In presence of chlorides and bromides the iodine in iodides may be precipitated and weighed as iodide of palladium.

Moisture in iodine is estimated by loss on exposing a weighed quantity of iodine in a capsule over a dish of sulphuric acid under a small bell-jar, or by adding to a weighed sample five or six times as much mercury or twice as much zinc, and a little water, drying and weighing. The product is the amount of metal employed plus that of the *dry* iodine in the sample.

BROMIDES.

Free bromine may be estimated by shaking with excess of solution of iodide of potassium, and then determining the equivalent quantity of liberated iodine by a standard solution of hyposulphite of sodium (p. 579).

The bromine in bromides may be precipitated and weighed as bromide of silver, the manipulations being the same as those for chloride of silver: 0.2 to 0.3 of pure bromide of potassium may be used for an experimental analysis.

Ammonii Bromidum, U. S. P.: "1 gm. of the powdered and dry salt, when completely precipitated by nitrate of silver, yields, if perfectly pure, 1.917 gm. of dry bromide of silver." *Calcii Bromidum*, U. S. P.: "1 gm of the dry salt, when completely precipitated by nitrate of silver, yields, if perfectly pure, 1.878 gm. of dry bromide of silver."

CYANIDES.

The hydrogen cyanide (hydrocyanic acid) is usually estimated volumetrically (*vide* p. 567).

From all soluble cyanides cyanogen may be precipitated by nitrate of silver after acidulating with nitric acid, the cyanide of silver collected on a tared filter, dried at 100° C., and weighed.

Of the official Diluted Hydrocyanic Acid it is stated that 100 grains (or 110 minims), precipitated by solution of nitrate of silver, yield 10 grains of dry cyanide of silver.

Cyanide of Silver.

		In 1 molec. wt.	In 100 parts.
Silver . . .	Ag . .	107.7 . .	80.55
Cyanogen .	CN . .	26.00 . .	19.45
		133.7	100.00

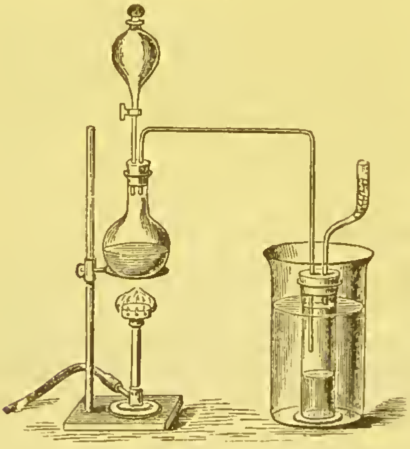
NITRATES.

Nitrates cannot be estimated by direct gravimetric analysis, none of the basylous radicals yielding a definite nitrate insoluble in water. With some difficulty they may be determined by indirect volumetric methods.

Process.—The following (Thorpe's) method depends upon the fact (Gladstone and Tribe) that when zinc upon which copper is deposited in a spongy form is boiled with water hydrogen is evolved. Thorpe found that in a solution containing nitrates the nascent hydrogen converts the whole of the nitrogen of the nitrates into ammonia, which may be collected and estimated. (The oxygen of the nitrate is simultaneously converted into water, the nitrate-metal into hydrate, and the zinc into hydrate of zinc. The power of the copper-zinc couple is considered to depend largely on the hydrogen absorbed by the finely-divided metal.)

An apparatus such as shown in Fig. 82 should be constructed. A flask (about 100 c.c.) is fitted with an India-rubber cork, perforated for a delivery-tube, which should be of strong glass tubing of about quarter-inch bore, and for a stoppered funnel, which should have about half the capacity of the flask. The whole is supported by a clamp or on wire-gauze. The outer jar shown in the figure should have a capacity of 2 or 3 litres, and the inner receiving-jar should be capable of holding 200 c.c. The latter is fitted with an India-rubber cork, perforated for the delivery-tube, and for another tube containing fragments of glass.

Fig. 82.



Estimation of Nitrates.

A few strips of clean zinc are boiled in a beaker with a 2-per cent. solution of sulphate of copper, the operation being repeated with a fresh portion of solution six consecutive times. A thick coating of finely-divided copper is deposited. The pieces of metal are well washed and introduced into the flask, which is then half filled with pure water. To avoid transference, the flask itself may be used instead of the beaker. The funnel also is filled with pure water. Into the inner receiver is put a little pure water very slightly acidulated with hydrochloric acid, and the glass fragments are also moistened with the dilute acid (to prevent possible loss of ammonia). Water is now placed around the inner receiver in the outer jar, and, the connections being sound, heat is applied with the view of freeing the apparatus itself from any trace of ammonia. When the contents of the flask are evaporated nearly to dryness, pure water is admitted from the funnel until the flask is again about half full (the funnel should be filled again at once), and the distillation carried on as before. This must be repeated until no further trace of ammonia is evolved, when the apparatus is ready for use. On each occasion that the apparatus is used it must be freed from ammonia in this way. A suitable quantity of the substance to be estimated is now introduced (in the case of potable waters the prepared solid residue from 100 c.c., with an added fragment of recently ignited lime, the size of a hemp-seed, to promote the evolution of the ammonia), and water added, if necessary, until the flask is half full. Heat is now applied, and the operation conducted in the manner already described until ammonia ceases to come over—a point which always occurs in the case of water-residues when the flask has been refilled twice and the distillate is about 100 c.c. The warm water from the upper part of the cooling-jar may be removed by a siphon or otherwise, cold water being introduced from time to time.

The ammonia being all evolved, disconnect the flask and receiver simultaneously (unless washing-bottle tubes are fitted), and treat the contents of the latter by the Nessler method, described on page 558.——Urea yields but traces of ammonia by this process, and neither the sulphates nor chlorides of the alkali-metals affect the result.——The method is only applicable to highly dilute solutions of nitrates, for with stronger solutions oxides of nitrogen are formed and escape.

Another process (Pelouze's improved by Fresenius) consists in adding the nitrate to an acid solution of a ferrous salt of known strength, and, when reaction is complete, estimating the amount of ferrous salt unattacked by volumetric solution of red chromate or of permanganate. Three molecular weights of converted ferrous salt indicate one molecular weight of nitric acid. Regeneration of nitric or nitrous acids by aërial oxidation of the nitric oxide evolved is prevented either by a current of carbonic acid gas or by using a closed flask in which is a *Bunsen valve* (*i. e.* a short attached piece of India-rubber tubing closed at the free extremity and having a sharp longitudinal slit in it a third of an inch long—a slit by which gases can escape, but cannot re-enter).

Potassii Nitras, U. S. P.: "If 1 gm. of the dried salt be moistened with 1 gm. of concentrated sulphuric acid, and the mixture be kept at a red heat until it ceases to lose weight, the residue should weigh 0.86 gm."

SULPHIDES.

Process 1.—Soluble sulphides (H_2S, NaHS, *e. g.*) may be determined volumetrically by adding to the aqueous liquid a measured excess of an alkaline solution of arsenic of known strength, neutralizing by hydrochloric acid, diluting to any given volume, filtering off the sulphide of arsenicum precipitated, taking a portion of the filtrate equal to half or a third of the original volume, and, after neutralizing by acid carbonate of sodium, estimating the residual arsenic by the standard iodine solution (*vide* p. 572). The process may be tried on a measured volume of sulphuretted hydrogen (the weight of which is easily calculated: 1 litre of hydrogen = 0.0896 gramme) absorbed by a strong solution of soda or potash.

Process 2.—Sulphur and sulphides may also be quantitatively analyzed by oxidizing to sulphuric acid and precipitating in the form of sulphate of barium. A couple of decigrammes of a pure metallic sulphide may be decomposed by careful deflagration with a mixture of chlorate of potassium and carbonate of sodium, the product dissolved in water, acidulated with hydrochloric acid, solution of chloride of barium added, and the precipitated sulphate of barium purified and collected as described in connection with the estimation of barium (p. 587). Many sulphides may be oxidized in a flask by chlorate of potassium and hydrochloric acid, and then precipitated by chloride of barium. Experimental determinations may also be made on a weighed fragment of sulphur, about 0.1 grm., cautiously fused with a solid caustic alkali, and the product oxidized while hot by the slow addition of powdered nitrate or chlorate of potassium, or, when cold, by treatment with chlorate of potassium and hydrochloric acid, and subsequent precipitation by chloride of barium.

Note.—Fusions performed by help of a gas-lamp must be carefully conducted, for any alkali that may creep over the side of a crucible will certainly absorb sulphurous acid from the products of combustion of the gas, and error result.

Process 3.—Soluble sulphides may also be treated with excess of an alkaline arsenite, arsenous sulphide be then precipitated by the addition of hydrochloric acid, and the precipitate collected and weighed with the usual precautions (*vide* p. 593).

Weights of Equivalent Quantities of Sulphur and its Compounds.

Sulphur	S	32
Sulphuretted hydrogen	H_2S	34
Sulphate of barium	$BaSO_4$	232.8
Arsenious sulphide	$(As_2S_3) \div 3$	82
Bisulphide of iron	$(FeS_2) \div 2$	60
Sulphide of lead	PbS	238.5

SULPHITES.

Sulphites are usually estimated volumetrically by a standard solution of iodine (*vide* p. 572). Sulphites insoluble in water are diffused in that menstruum, hydrochloric acid added, and the iodine solution then dropped in.

If necessary, sulphites may be estimated gravimetrically by oxidation and precipitation in the form of sulphate of barium.

SULPHATES.

These salts are always precipitated and weighed as sulphate of barium, the manipulations being identical with those performed in the determination of barium by means of sulphates (*vide* p. 587). The purity of Sulphate of Sodium (*Sodii Sulphas*, U. S. P.), and the presence of not more than a given amount of sulphuric acid in vinegar (*Acetum*, B. P.), are directed, in the British Pharmacopœia, to be ascertained by this process. Ten grains of sulphate of sodium yield 7.23 of sulphate of barium. Five ounces of vinegar should yield not more than about one-third of a gramme of sulphate of barium.

The amount of free sulphuric acid or hydrochloric acid in vinegar, lemon-juice, lime-juice, etc. may also be ascertained volumetrically by adding a known quantity of standard solution of soda, evaporating to dryness, incinerating, dissolving in water, and, by standard acid, estimating the quantity of soda still remaining free. The soda lost indicates the amount of free mineral acid (Hehner). Thresh estimates the chlorine in a sample of vinegar, adds a known additional amount of chlorine, preferably in the form of chloride of barium, evaporates, ignites; treats with water, adds bicarbonate of sodium to remove excess of barium, filters, and again estimates the chlorine. A loss of 70.8 of chlorine (Cl_2) indicates 98 of free sulphuric acid (H_2SO_4). The method of estimating free sulphuric, nitric, or hydrochloric acid proposed by Spence and Esilman is founded on their power of decolorizing a standard solution of ferric acetate.

Proportional Weights of Equivalent Quantities of Sulphates.

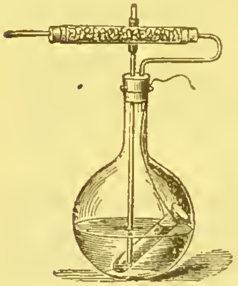
The sulphuric radical	SO_4	96
Sulphuric acid	H_2SO_4	98
Sulphate of barium	$BaSO_4$	232.8

CARBONATES.

Carbonates are usually estimated by the loss in weight they undergo on the addition of a strong acid.

Process 1.—A small light flask is selected—of such a size that it can be conveniently weighed in a delicate balance. Two narrow glass tubes are fitted to the flask by a cork; the one straight, extending from about two or three centimetres above the cork to the bottom of the flask; the other cut off close to the cork on the inside and curved outward, so as to carry a thin drying-tube horizontally above the flask. (See Fig. 83.) The drying-tube is nearly filled with small pieces of chloride of calcium, a plug of cotton-wool preventing escape of any fragments at either end, and is attached by a pierced cord to the free extremity of the curved tube of the flask. A weighed quantity of any pure soluble carbonate is placed in the flask, a little water added, a miniature test-tube containing sulphuric acid lowered into the flask by a thread and supported so that the acid may not flow out. the cork inserted, the outer end of the piece of the straight glass tube closed by a fragment of cork or wax, and the whole weighed. The apparatus is then inclined so that the oil of vitriol and carbonate may slowly react; carbonic acid gas is evolved and escapes through the horizontal tube, any moisture being retained by the chloride of calcium. When effervescence has ceased, the gas still remaining in the vessel is sucked out; this is accomplished by adapting a piece of India-rubber tubing to the end of the drying-tube, removing the small plug from the straight tube, and aspirating slowly with the mouth for a few minutes. If the heat produced by the action of oil of vitriol and solution is considered insufficient to expel all the carbonic acid from the liquid, the plug is again inserted in the tube and the contents of the flask gently boiled for some seconds. When the apparatus is nearly cold more air is again drawn through it, and the whole finally weighed. The loss is due to carbonic acid gas (CO_2), from the weight of which that of any

Fig. 83.



Estimation of Carbonates.

carbonate is ascertained by calculation. Carbonates insoluble in water may be attacked by hydrochloric instead of sulphuric acid; granulated mixtures of carbonates and powdered tartaric or citric acid by enclosing the preparation in the inner tube and placing water in the flask, or *vice versâ.* The apparatus also may be modified in many ways to suit the requirements, convenience, or practice of the operator.

Process 2.—Carbonates from which carbonic acid gas is evolved by heat may be estimated by the loss they experience on ignition.

Process 3.—Free carbonic acid gas may be absorbed by a solid stick of potash or a strong alkaline solution, the loss in volume of the gas or mixture of gases indicating the amount originally present.

Weights of Equivalent Quantities of Carbonic Acid Gas and certain Carbonates.

Carbonic acid gas	CO_2	44
Carbonic acid	H_2CO_3	62
Anhydrous carbonate of sodium .	Na_2CO_3	106
Crystalline carbonate of sodium .	$Na_2CO_3,10H_2O$. .	286
Anhydrous carbonate of potassium .	K_2CO_3	138
Crystalline carbonate of potassium .	$K_2CO_3+16\%$aq.164.	285
Carbonate of calcium	$CaCO_3$	100

OXALATES.

Process 1.—The oxalic radical is usually precipitated in the form of oxalate of calcium and weighed as carbonate, the manipulations being identical with those observed in the estimation of calcium (*vide* p. 588). The experiment may be performed on 0.3 or 0.4 grm. of pure crystallized oxalic acid, 126 parts of which should yield 100 of carbonate of calcium.

Process 2.—Oxalates may also be determined by conversion of their acidulous radical into carbonic acid gas, and observation of the weight of the latter. The oxalate, water, and excess of black oxide of manganese are placed in the carbonic acid apparatus (page 606), a tube containing oil of vitriol lowered into the flask, the whole weighed, and the operation completed as for carbonate. From the following equation it will be seen that every 88 parts of carbonic acid gas evolved indicate the presence of 126 parts of crystallized oxalic acid or an equivalent quantity of other oxalate:—

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2.$$

The black oxide of manganese used in this experiment must be free from carbonates. The amount of materials employed is regulated by the size of the vessels.

PHOSPHATES.

Process 1.—From phosphates dissolved in water the phosphoric radical may be precipitated and weighed in the form of pyrophosphate of magnesium, the details of manipulation being similar to those observed in estimating magnesium (*vide* p. 589). Half a gramme or rather more of pure dry crystallized phosphate of sodium may be employed in experimental determinations. The official phosphate of ammonium (*Ammonii Phosphas*, U. S. P.) is quantitatively analyzed by this method. "2 gm. of the salt, dissolved in water and precipitated with test-mixture of magnesium, yields a crystalline precipitate, which, when washed with diluted water of ammonia, dried, and ignited, should weigh 1.68 gm." Half a gramme or less is a more convenient quantity if the operations be conducted with care. Solution of ammonia-sulphate of magnesium (U. S. P.) is prepared by dissolving 1 part of sulphate of magnesium, 2 of chloride of ammonium, and 4 of solution of ammonia (10-per cent. NH_3) in 8 of distilled water; such a solution is of considerable use if several phosphoric determinations are about to be made.

Process 2.—Free phosphoric acid is most readily determined as phosphate of lead (Pb_32PO_4). Of the official solution of phosphoric acid it is stated that "on pouring 5 gm. of phosphoric acid upon 10 gm. of oxide of lead free from carbonate of lead and from moisture, evaporating and igniting, a residue will be obtained which should weigh 11.81 gm." In the case of the diluted acid, 5 gm. with 5 of lead oxide should yield 5.36. The oxide of lead must be quite pure: it should be prepared by digesting red lead in warm dilute nitric acid, washing, drying, and heating a resulting puce-colored plumbic oxide in a covered porcelain crucible. The increase in weight obtained on evaporating a given amount of solution of phosphoric acid with a known weight of perfectly pure oxide of lead (PbO) may be regarded as entirely due to phosphoric anhydride (P_2O_5),

$$3PbO + P_2O_5 = Pb_32PO_4,$$

the actual reaction being

$$3PbO + 2H_3PO_4 = Pb_32PO_4 + 3H_2O.$$

From these equations and the table of atomic weights (*vide*

Appendix) the percentage of phosphoric acid (H_3PO_4) in any specimen of its solution may be easily calculated.

Process 3.—The strength of pure solution of phosphoric acid may be ascertained by specific gravity and reference to Tables.

Process 4.—Bone-earth, "superphosphate," the *Calcis Phosphas* of pharmacy, and other forms of phosphate of calcium known to be tolerably free from iron or aluminium, may be estimated by treating about half a gramme with hydrochloric acid somewhat diluted, filtering if necessary, warming, precipitating with excess of ammonia, collecting the precipitate (Ca_32PO_4), washing, drying, igniting, and weighing. "*Calcis Phosphas,*" if pure, will in this process lose no weight.

Process 5.—Insoluble phosphates in ashes, manures, etc. are treated as follows: A weighed quantity of the material (1.0 to 10.0 grm.) is digested in hydrochloric acid diluted with three or four times its bulk of water; filtered (insoluble matter and filter being thoroughly exhausted by water); ammonia added to the filtrate and washings until, after stirring, a faint cloudy precipitate is perceptible; solution of oxalic acid dropped in until, after agitation for a few minutes, the opalescence is destroyed; oxalate of ammonia next added, the whole warmed, oxalate of calcium removed by filtration, and the filtrate concentrated if very dilute; the liquid treated with citric acid in such quantity that ammonia when added in excess gives a clear *lemon-yellow* solution (Warington), magnesian mixture poured in (as in Process 1), and the precipitate of ammonio-magnesian phosphate collected, washed, dried, and weighed, as already described in connection with the estimation of magnesium.

Relative Weights of Equivalent Quantities of Phosphoric Compounds.

Phosphoric acid	H_3PO_4	98
Pyrophosphate of magnesium .	($Mg_2P_2O_7 = 222$)$\div 2 =$	111
Phosphate of lead	($Pb_32PO_4 = 811$) $\div 2 =$	405.25
Phosphoric anhydride . . .	($P_2O_5 = 142$) $\div 2 =$	71
Phosphate of calcium . . .	($Ca_32PO_4 = 310$) $\div 2 =$	155
Superphosphate of calcium .	($CaH_42PO_4 = 234 \div 2 =$	117

QUESTIONS AND EXERCISES.

1044. What quantity of pure rock-salt is equivalent to 4.2 parts of chloride of silver? *Ans.* 1.714.

1045. State the percentage of real iodide of potassium contained in a sample of which 8 parts yield 10.9 of iodide of silver. *Ans.* 96.3.

1046. What is the strength of a solution of hydrocyanic acid 10 parts of which, by weight, yield .9 of cyanide of silver. *Ans.* 1.87 per cent.

1047. How are nitrates quantitatively estimated?

1848. By what processes may the strength of sulphides be determined?

1049. How much real sulphate of sodium is contained in a specimen 10 parts of which yield 14.2 of sulphate of barium. *Ans.* 86.61 per cent.

1050. Give details of the operations performed in the quantitative analysis of carbonates.

1051. What amount of carbonic acid gas should be obtained from 10 parts of acid carbonate (or bicarbonate) of potassium? *Ans.* 4.4 parts.

1052. To what operation and what proportion of materials does the following equation refer?—

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2.$$

1053. Explain the lead process for the estimation of phosphoric acid in the official solution.

1054. State the amount of superphosphate of calcium equivalent to 7.6 parts of pyrophosphate of magnesium. *Ans.* 8.01.

SILICATES.

Silica (SiO_2) may be separated from alkaline silicates, or from silicates decomposable by hydrochloric acid, by digesting the substance in hydrochloric acid at a temperature of 70° or 80° C. until completely disintegrated, evaporating to dryness, heating in an air-bath, again moistening with acid, diluting with hot water, filtering, washing, drying, igniting, and weighing.

ESTIMATION OF WATER.

Water and other matters readily volatilized are most usually estimated by the loss in weight which a substance undergoes on being heated to a proper temperature. Thus, in the British Pharmacopœia crystalline gallic acid ($H_3C_7H_3O_5,H_2O$) is stated to lose 9.5 per cent. of its weight at a temperature of 100° C., oxalate of cerium ($CeC_2O_4,3H_2O$) 52 per cent. on incineration, carbonate of potassium about 16 per cent. on exposure to a red heat, sulphate of quinine ($2C_{20}H_{24}N_2O_2,H_2SO_4,7H_2O$) 14.4 per cent. at 100° C., arseniate of sodium ($Na_2HAsO_4,7H_2O$) 40.38 per cent. at 149° C., carbonate of sodium ($Na_2CO_3,10H_2O$) 60.3 per cent., phosphate of sodium ($Na_2HPO_4,12H_2O$) 63 per cent., and sulphate of sodium ($Na_2SO_4,10H_2O$) 55.9 per cent. at a low red heat; oxide of bismuth heated to incipient redness should not diminish in weight.

Process.—One or two grammes of substance is sufficient in experiments on desiccation, the material being placed in a watch-glass, covered or uncovered porcelain crucible, or other vessel, according to the temperature to which it is to be exposed. Rapid desiccation at an exact temperature may be effected by introducing the substance into a tube having somewhat the shape of the letter U, sinking the lower part of the tube into a liquid kept at a definite temperature by aid of a thermometer, and drawing or forcing a current of dry air slowly through the apparatus. Substances liable to oxidation may be desiccated in a current of dried carbonic acid gas. The weights of the U-tube before and after the introduction of the salt, and after desiccation, give the amount of water sought. In all cases the material must be heated until it ceases to lose weight. Occasionally it is desirable to estimate water directly by conveying its vapor in a current of air through a weighed tube containing chloride of calcium and reweighing the tube at the close of the operation; the increase shows the amount of water.

Note.—Highly dried substances rapidly absorb moisture from the air; they must therefore be weighed quickly, enclosed, if possible, in tubes (p. 583), a pair of clamped watch-glasses, or a crucible having a tightly fitting lid.

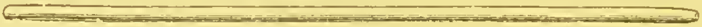
CARBON, HYDROGEN, OXYGEN, NITROGEN.

The quantitative analysis of animal and vegetable substances is either *proximate* or *ultimate.* Proximate quantitative analysis includes the estimation of water, oil, albumen, starch, cellulose, gum, resins, alkaloids, acids, glucosides, ash. It requires the application of much theoretical knowledge and manipulative skill, and cannot well be studied except under the guidance of a tutor. One of the best of the published works on the subject is by Rochleder, a translation of whose monograph will be found in the *Pharmaceutical Journal*, vol. i. 2d ser. pp. 562, 610; vol. ii. 2d ser. pp. 24, 129, 160, 215, 274, 420, 478. Another is a small book by Professor A. B. Prescott, *Outlines of Proximate Organic Analysis*, Van Nostrand, New York.

Ultimate quantitative organic analysis can only be successfully accomplished with the appliances of a well-appointed laboratory—a good balance, a gas-furnace giving a smokeless flame (7 or 8 centimetres wide and 70 or 80 centimetres long), special forms of glass apparatus, etc. *The theory of the operation* is simple: A weighed quantity of a substance is burnt to carbonic acid gas ($CO_2 = 44$) and water ($H_2O = 18$), and these products collected and weighed; 12 parts in every 44 of carbonic acid gas ($= \frac{3}{11}$) are carbon, 2 in every 18 of water ($= \frac{1}{9}$) are hydrogen; nitrogen if present escapes as gas. If nitrogen be a constituent, more of the substance is strongly heated with a mixture of the hydrates of sodium and calcium; these bodies then split up into oxides, oxygen, and hydrogen; the oxygen burns the carbon of the substance to carbonic acid gas, its hydrogen and nitrogen appearing as water and ammonia respectively; the carbonic acid and water are disregarded, the ammonia collected and weighed in the form of a double chloride of platinum and ammonium ($PtCl_4 2NH_4Cl = 442.8$), of which 28 parts in every 442.8 ($= \frac{1}{16}$) are nitrogen. The difference between the sum of the weights of hydrogen and carbon, and the weight of substance taken, is the proportion of oxygen in the body, supposing nitrogen to be absent. If nitrogen is present, the difference between the sum of the percentage of carbon, hydrogen, and nitrogen, and 100, is the percentage of oxygen. Shortly, carbon is estimated in the form of carbonic acid gas, hydrogen as water, nitrogen as ammonia, and oxygen by loss.

The following is the outline of the necessary manipulation:—The source of the oxygen for the combustion of carbon and hydrogen is black oxide of copper in coarse powder. 200 or 300 grammes of this material are heated in a crucible to low redness for a short time to expel every trace of moisture; then transferred to store-tubes (Fig. 84) resembling test-tubes, half a metre long, and having a slightly narrowed mouth, the tube being held in a cloth to protect the hand while the hot oxide is being directly introduced into the mouth of the tube by a scooping motion. As soon as the well-corked tube is cool, the oxide is poured, portion by portion, into a similar tube (the combustion-tube), but somewhat longer, drawn out to a quill (bent upward nearly to a right angle) at one end and not constricted at the mouth. Two such tubes are readily made by softening in the blowpipe-flame two or three centimetres of the central part of a tube about a metre long, and drawing the halves of the tube apart, as shown in the following engraving (Fig. 85). The tubes are separated by melting the glass in the middle of the quilled portion. A few decigrammes of fused chlorate of potassium should first be dropped into the tube. After ten or fifteen centimetres of oxide have been poured in, about a decigramme of the substance to be analyzed is dropped down the tube, then a few grammes of oxide, then another decigramme of substance, then more oxide, until three or four decigrammes of the body under examination have been added. The fifteen or twenty centimetres of alternate layers are next thoroughly mixed by a long copper wire having a short helix; more oxide is introduced, the wire cleansed by twisting the

Fig. 84.



helix about in the pure oxide, and a plug of dry asbestos finally placed on the top of the oxide at about five centimetres from the mouth of the tube; the tube is then securely corked and set aside. The substance operated on may be pure white sugar, powdered and dried; the tube in which it is contained is weighed before and after the removal of a portion for combustion; the loss is the quantity employed in the experiment. The combustion-furnace may be such as shown on page 597. If the furnace is very powerful or the combustion-tube not of the hardest glass, the tube should be enclosed in wire-gauze the elasticity of which has been destroyed by heating to redness. If the substance under experiment contains nitrogen, the plug of asbestos must be displaced by one of copper turnings, which serves to reduce any oxides of nitrogen, and thus ensure the escape of nitrogen itself. The *water* produced when the prepared tube is heated is collected in a small U-tube containing pieces of chloride of calcium, or pumice-stone moistened with sulphuric acid (Fig. 86); the *carbonic acid gas* in a series of bulbs (Fig. 86) containing solution of potash (sp. gr. about 1.27). These bulbs may be purchased at any apparatus-shop. The chloride-of-calcium tube is fitted by a good cork to the combustion-tube, the potash-bulbs by a short piece of India-rubber tubing to the chloride-of-calcium tube. The potash-bulbs may carry a short light tube containing a rod of caustic potash three or four centimetres long; this serves to arrest any moisture that might be carried away from the solution of potash by the dried expanded air which escapes during the operation. The combustion-tube having been placed in the furnace,

Fig. 85.

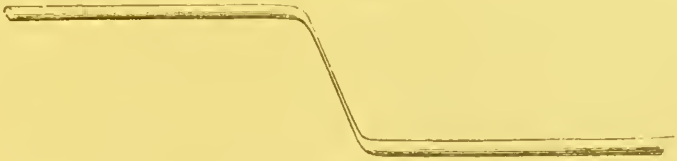
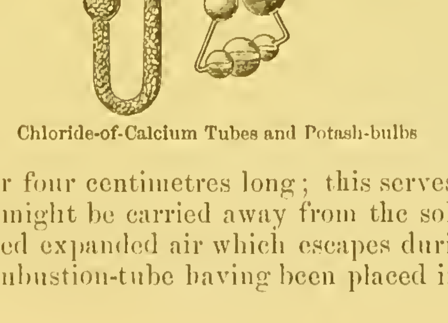


Fig. 86.



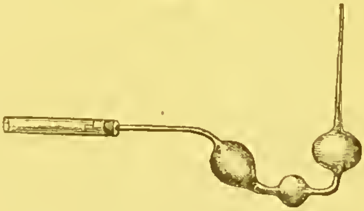
Chloride-of-Calcium Tubes and Potash-bulbs and the drying-tube and potash-bulbs weighed and detached, the gas is lit under the asbestos, and, when the tube is red hot, the flame slowly extended until nearly the whole tube is at the same temperature, the operation being conducted at such a rate that bubbles of gas escape through the potash-bulbs at about the rate of one per second. When no more gas passes, the extremity of the tube containing the chlorate of potassium is gently heated until oxygen ceases to be evolved; the quilled extremity of the combustion-tube is then broken, and air, dried and freed from carbonic acid, drawn slowly through the apparatus by suction through an India-rubber tube fixed on the free end of the potash-bulbs; perfect combustion of carbon and removal of all carbonic acid gas are thus ensured. The drying-tube and bulbs are disconnected and weighed, the increase in weight due to carbonic acid gas and water respectively noted, and the percentages of carbon, hydrogen, and (by loss) oxygen calculated. This method is that of Liebig, with modification by Bunsen; good combustion-furnaces are those known as Hofmann's and Griffin's.

Chromate of lead can be used for combustion in place of oxide of copper. Its advantages are, its less hygroscopic nature, and the greater readiness with which it yields its oxygen to organic bodies when heated with them. It must not, however, be used with bodies containing nitrogen, since it would convert so large a proportion of the nitrogen into nitric oxide or higher oxide of nitrogen that it would be necessary to use an inconveniently long layer of copper turnings to reduce these oxides, and so prevent their absorption in the series of bulbs containing the solution of potash. Organic bodies, however, containing sulphur, bromine, iodine, or chlorine are burnt with advantage by means of chromate of lead. If oxide of copper were used with bodies containing sulphur, it would be necessary to place an additional tube containing peroxide of lead between the chloride-of-calcium tube and the potash-bulbs in order to absorb the sulphurous anhydride formed; this is entirely obviated by using chromate of lead, which itself retains the whole of the sulphur. Again, if bodies containing chlorine, iodine, or bromine are burnt by means of oxide of copper, then volatile chloride, iodide, or bromide of copper is formed. and. collecting in the chloride-of-calcium tube, vitiates the result with regard to the hydrogen; by using chromate of lead, however, the chlorine, iodine, and bromine are respectively retained in the combustion-tube as chloride, bromide, and iodide of lead.

In order to render the chromate fit for use, it is first fused and poured out on a clean iron plate; when cool it is powdered, and heated in a long tube throughout its whole length, while air, dried by passing through chloride of calcium or strong sulphuric acid, is drawn over it; when the color of the chromate changes to brown the heat can be withdrawn and the extremity of the tube farthest from the drying apparatus closed, so that the air in passing into the tube on cooling may be quite dry; when cool the drying-tube is removed, the extremity securely corked, and the carbonate of lead is ready for direct transference to the combustion-tube.

The general manipulations for substances containing nitrogen resemble the foregoing so far as the use of a combustion-tube and furnace and collection of the ammoniacal gas are concerned. The combustion-tube must be quilled at one end, and about a third of a metre long. The soda-lime is made by slaking quicklime with a solution of soda, of such a strength that about two parts of quicklime shall be mixed with one of hydrate of sodium, drying the product, heating to bright redness, and finally powdering; it should be preserved in a well-closed bottle. Some of the soda-lime is introduced into the tube, then layers of substance and soda-lime, mixture effected by a wire, more soda-lime added, and lastly a plug of asbestos. Bulbs (Fig. 87), known as those of Will and Varrentrapp (the originators of the method), containing hydrochloric acid of about 25 per cent., are then fitted by a cork, and the tube heated in a furnace to a not too bright red heat, or some of the produced ammonia may be decomposed. When gas ceases to pass and combustion is considered to be *quite* complete, the tube is allowed to cool somewhat. The quill is then broken, and aspiration continued slowly until ammoniacal gas may be considered to have been all absorbed by the acid. The bulls are disconnected, their contents and rinsings poured into a small dish, solution of perchloride of platinum added, and the operation completed, as in the estimation of ammonium and potassium salts (*vide* pp. 584 and 586).

Fig. 87.



Nitrogen-bulbs.

Liquids are analyzed by a similar method to that adopted for solids, volatile liquids being enclosed in small bulbs having a long quill. These are weighed previously to and after the introduction of the liquid; just before being dropped into the combustion-tube the quill is broken.

Formulæ.—From the percentage composition of an organic substance an empirical formula may be deduced by dividing the weight of each constituent by its atomic weight, and converting the product into the simplest whole numbers; a rational formula by ascertaining the proportion in which the substance unites with a radical or body having a known combining proportion, etc. (*vide* p. 428).

Chlorine, *bromine*, or *iodine* contained in an organic substance is usually estimated by heating to redness a given weight of the material with ten times as much pure lime in a combustion-tube. Chloride, bromide, or iodide of calcium is thus produced. While still hot the tube is plunged into water, the mixture of broken glass and powder treated with pure diluted nitric acid in very slight excess; the filtered liquid precipitated by nitrate of silver, and the chloride, bromide, or iodide of silver collected, washed, dried, and weighed.

Sulphur, *phosphorus*, and *arsenicum* in organic salts may be estimated by gradually heating in a combustion-tube 1 part of the substance with a mixture of 10 parts nitre, 2 dried carbonate of sodium (in order to moderate deflagration), and 30 chloride of sodium. The product is dissolved in water acidulated by nitric acid, the sulphuric radical precipitated and estimated as sulphate of barium, the phosphoric and arsenic radicals as ammonio-magnesium phosphate or arseniate.

QUININE OR QUINIA.

De Vrij's Method for the Separation of the Mixed Alkaloids from Cinchona-bark.—This is the method adopted for the assay of cinchona-bark in the United States Pharmacopæia: Twenty grammes of powdered and sifted bark, dried at 100° C., are mixed with milk of lime made of 5 grammes of dry slaked lime and 50 grammes of water. This mixture is slowly dried, and when entirely dry heated in a flask with 200 c.c. of very strong alcohol (about 95 per cent.) till it boils. After well shaking, the clear liquid is poured by degrees into a percolating tube. The flask is then washed with 200 c.c. more of the same alcohol, and the liquid passed through the percolator. After this has run through, a little clear, colorless liquid may be further collected by pouring into the percolator successive small quantities of distilled water. The united clear liquors are now slightly acidulated with weak sulphuric acid, whereby a precipitate of sulphate of calcium is formed. When this has subsided the greater part of the liquid may be decanted and the rest passed through a small filter. From the clear solution most of the spirit is distilled off, the residue poured into a capsule, and the still washed with a little weak spirit, the washings being added to the liquid in the capsule. The capsule is now heated on a water-bath till free from alcohol, and the remaining liquor, which contains all the alkaloids in the form of acid sulphates, is, after cooling, passed through a small filter. On the filter remains a mixture of quinovine* and fatty substances, which must be repeatedly washed with water slightly acidulated with sulphuric acid, till the washings are no longer rendered turbid by caustic soda. The filtrate, concentrated over a water-bath, is, while *still warm*, precipitated by a large excess of caustic soda. This precipitation from a warm solution has the advantage of rendering the alkaloids less voluminous, and therefore capable of being more easily washed. (Should the alkaloids melt, as is sometimes the case under this treatment, the liquid must be cooled and the fused alkaloids carefully powdered before proceeding to the next step of the process.) The precipitate is next placed on a small filter, washed with the smallest possible quantity of distilled water (sufficient to remove the soda-salt without dissolving the quinine, etc.); the filter is laid on blotting-paper, and this is renewed until the mixed alkaloids can easily be removed from the filter without adhering to it: this can be done before they are quite dry, but requires some practice. They are then heated in a tared capsule on a water-bath till they cease to lose weight. The observed weight multiplied by five gives the percentage of mixed alkaloids in the bark. The intensely yellow alkaline liquor separated from the alkaloids contains still a small quantity of quinovine, which can be separated by acidifying with hydrochloric acid.

Assay of Mixed Alkaloids for Quinine.—The official (U.S.P.) method is as follows: "To the total alkaloids from 20 grammes of cinchona, previously weighed, add distilled water acidulated with diluted sulphuric acid until the mixture remains for ten or fifteen minutes after digestion just distinctly acid to test-paper. Transfer to a weighed beaker, rinsing with distilled water, and adding of this enough to make the whole weigh *seventy times* the weight of the alkaloids. Add now, in drops, solution of soda previously well diluted with distilled water until the mixture is exactly neutral to test-paper. Digest at 60° C. (140° F.) for five minutes, then cool to 15° C. (59° F.), and maintain at this temperature for half an hour. If crystals do not appear in the glass vessel, the total alkaloids do not contain quinine in quantity over *eight per cent.* of their weight (corresponding to *nine per cent.* of sulphate of quinine, crystallized). If crystals appear in the mixture, pass the latter through a filter not larger than necessary, prepared by drying two filter-papers of two to three and a half inches (5 to 9 centimetres) diameter, trimming them to an equal weight, folding them separately, and placing one within the other so as to make a plain filter fourfold on each side. When the liquid has drained away, wash the filter and contents with distilled water of a temperature of 15° C. (59° F.), added in small portions, until the entire filtered liquid weighs *ninety times* the weight of the alkaloids taken. Dry the filter, without separating its folds, at 60° C. (140° F.), to a constant weight, cool, and weigh the inner filter and contents, taking the outer filter for a counterweight. To the weight of effloresced sulphate of quinine so obtained add 11.5 per cent. of its amount (for water of crystallization), and add 0.12 per cent. of the weight of the entire filtered liquid (for solubility of the crystals at 15° C. or 59° F.). The sum in grammes, multiplied by *five*, equals the percentage of crystallized sulphate of quinine equivalent to the quinine in the cinchona."

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* This is strictly a mixture of quinovine and quinovic acid, but, as quinovine is by far the larger constituent, I actually prefer the name of quinovine for the mixture.—*De Vrij.*

De Vrij's Method for the Separation and Quantitative Determination of All the Different Cinchona Alkaloids.—This is based upon the following facts (nomenclature adopted by the Quinological Congress of Amsterdam, 1877):—

1. The great solubility of quinine and amorphous alkaloids in ether, and the *relative* insolubility of quinidine, cinchonidine, and cinchonine in this liquid.

2. The great solubility of the iodosulphate of the amorphous alkaloid in alcohol of at least 90 per cent., and the very slight solubility of the iodosulphate of quinine (Herapathite) in the same.

3. The great difference in solubility between the tartrate of cinchonidine and the tartrates of cinchonine and quinidine—the first being soluble in 1265 parts of water at 10° C., the second in 35.6 parts of water at 16° C., and the third in 38.8 parts of water at 15° C.

4. The great difference in solubility between the hydriodate of quinidine and the hydriodates of cinchonidine and cinchonine in water and alcohol. One part of hydriodate of quinidine requires 1250 parts of water at 15° C. or 110 parts of alcohol; the same salt of cinchonidine, 110 parts of water or 3 parts of alcohol; and that of cinchonine, 128 of water or 3 of alcohol.

These facts are applied to the separation and determination of the different cinchona alkaloids in the following manner:—

A. *Determination of Quinine.*—1. *Preparation of the Iodosulphate of Chinioidin.* One part of commercial quinoidin (Sulphate of Chinoidin is identical with Sulphate of Amorphous Quinine, prepared according to Dr. De Vrij's process by Messrs. Howard & Sons, Stratford, London) is heated on a water-bath with two parts of benzol, whereby the quinoidin is partly dissolved. The cold clear benzol solution is shaken with an excess of weak sulphuric acid, whereby a watery solution of acid sulphate of chinioidin is obtained. After ascertaining in a small part of this solution the amount of amorphous alkaloid contained in it, so that its whole quantity in the solution may be known, the clear solution is poured into a large capsule. For every 2 parts of amorphous alkaloids contained in the solution, 1 part of iodine and 2 parts of iodide of potassium are dissolved in water. This solution is *slowly* added *under continuous stirring* to the liquid in the capsule, so that no part of it comes into contact with an *excess* of iodine. By this addition an orange-colored flocculent precipitate is formed of iodosulphate of chinioidin, which either spontaneously or by a slight elevation of temperature collapses into a dark brown-red colored resinous substance, whilst the supernatant liquor becomes clear and slightly yellow-colored. This liquor —which, if the prescription is strictly followed, *must* still contain some amorphous alkaloid as a proof that no excess of iodine has been used—is poured off and the resinous substance is washed by heating it on a water-bath with distilled water. After washing, the resinous substance is heated on the water-bath till all the water has been evaporated. It is then soft and tenacious at the temperature of the water-bath, but becomes hard and brittle after cooling. One part of this substance is now heated with 6 parts of alcohol of 92 to 95 per cent. on a water-bath, and is thus dissolved, and the solution allowed to cool. In cooling, a part of the dissolved substance is separated. The clear dark brown-red colored solution is evaporated on a water-bath, and the residue dissolved in 5 parts of *cold* alcohol. This second solution leaves a small part of insoluble substance. The clear dark brown-red colored solution obtained by the separation of this insoluble matter either by decantation or filtration constitutes the reagent which, under the name of "iodosulphate of chinioidin," Dr. De Vrij uses both for the qualitative and quantitative determination of the *crystallizable* quinine in barks.

2. *Application of the Reagent.* To determine the quantity

of quinine contained in the mixed alkaloids obtained from a cinchona-bark, 1 part of these alkaloids* is dissolved in 20 parts of alcohol of 92 to 95 per cent., containing 1·5 per cent. of H_2SO_4,† to obtain an alcoholic solution of the acid sulphates of the alkaloids, and this solution is diluted with 50 parts of pure alcohol. From this solution the quinine is separated *at the ordinary temperature* by adding carefully, by means of a pipette, the above-mentioned solution of iodosulphate of chinioidin as long as a dark brown-red precipitate of iodosulphate of quinine (Herapathite) is formed. As soon as all the quinine has been precipitated, and a slight‡ excess of the reagent has been added the liquor acquires an intense yellow color, The beaker§ containing the liquor with the precipitate is now covered by a watch-glass, and heated till the liquid begins to boil and all the precipitate is dissolved. The beaker is then left to itself, and in cooling the Herapathite is separated in the well-known beautiful crystals. After twelve hours' rest the beaker is weighed to ascertain the amount of liquid which is necessary in order to be able to apply later the necessary correction, for although the quinine-Herapathite is very slightly soluble in cold alcohol, it is not insoluble.‖ The clear liquid is poured off¶ as far as possible on a filter, leaving the majority of the crystals in the beaker, which is now weighed again to ascertain the amount of liquid, which is noted down. The few crystals on the filter are now washed down in the beaker, and as much alcohol added as is necessary to redissolve all the crystals at the boiling-point. The object of this redissolving is to be absolutely certain that by surface attraction no trace of iodosulphate of cinchonidine has adhered to the crystals of Herapathite, for these traces, if present, will remain dissolved after the recrystallization. After perfect cooling the weight of the beaker is ascertained again, the crystals of Herapathite carefully collected on a small filter, and the empty beaker weighed again. The difference in weight will indicate the amount of liquor which is added to that of the first liquor, and from the sum of this addition the necessary correction is calculated. If the operation is effected at a temperature of 16° C., the weighed quantity of the two combined liquors will indicate the correction if multiplied by 0.125 and divided by 100. If the temperature be lower or higher, the solubility of Herapathite at that temperature must be ascertained by experiment, which can be easily performed by a standard solution of hyposulphate of sodium, as 21.58 parts of iodine found by this reagent indicate 100 parts of Herapathite. The Herapathite collected on the filter is thoroughly washed with a saturated alcoholic solution of pure Herapathite,* and after this washing is completed the liquid retained by the crystals is expelled as much as possible by slightly knocking the sides of the funnel. The filter is then taken from the funnel and laid upon blotting-paper, often renewed, to take away as quickly as possible the still adhering liquid. As soon as the filter is air-dry the crystals of Herapathite can be completely removed from the filter and dried on a water-bath in one of a couple of large watch-glasses closing tightly upon each other, so that the weight of the substance contained in the glass may be taken without the access of the air. If, after repeatedly weighing, the weight remains constant, it is noted down, and to it is added the product of the calculated correction. The sum of this addition is the total amount of iodosulphate of quinine obtained from the mixed alkaloids subjected to the operation, and from this weight the amount of quinine can be calculated by the use of Jörgensen's formula: $4C_{20}H_{24}N_2O_2,3H_2SO_4,2HI,I_4$. According to this formula, 1 part of Herapathite dried at 100° C. represents 0.55055 part of pure anhydrous quinine.

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* One gramme is a sufficient quantity.

† This quantity is quite sufficient to transform the alkaloids into acid sulphates, for an excess of acid would increase the solubility of the Herapathite.

‡ If cinchonidine is present in large quantity—as, for instance, in the alkaloids obtained from succirubra-bark—the estimation of this slight excess requires a great deal of practical experience, which cannot be acquired without having studied the action of the reagent on a solution of pure cinchonidine in the quantity mentioned of pure and acid alcohol. In manipulating the alkaloids of succirubra-bark, it often happens that the first drops of the reagent, instead of producing a precipitate of quinine-Herapathite, form an orange-colored gelatinous precipitate. In this case the further addition of the reagent is stopped and the beaker slightly heated, whereby the precipitate immediately disappears. In rubbing, then, the sides of the beakers with a glass rod, the quinine-Herapathite appears, and then the reagent can be safely added again.

§ The conical form of beaker, commonly in use, is peculiarly adapted for this purpose.

‖ According to the experiments of Professor Jörgensen, 100 parts of a saturated solution of Herapathite in alcohol of 90 per cent. at a temperature of 16° C. contain 0.125 parts of Herapathite.

¶ Before pouring off the whole quantity, it is safe to ascertain with a small portion of it if the necessary quantity of the reagent has been added.

B. *Determination of the Other Alkaloids.*—Two grammes of the pulverized mixed alkaloids are dissolved in weak hydrochloric acid to obtain a slightly alkaline solution measuring 70 c.c. By adding 1 gramme of Rochelle salt to this solution the tartrates of quinine and cinchonidine are separated; these are collected on a filter, washed with a little water, and dried on a water-bath. One part of these tartrates represents .80844 of quinine and cinchonidine: from the amount of these alkaloids thus found the amount of quinine already ascertained is subtracted, the remainder representing the cinchonidine present. In the filtrate from the tartrates quinidine (if present) is precipitated by a concentrated solution of potassium iodide; one part of the dried hydriodate representing .86504 of crystallized quinidine. The remaining solution is treated with caustic soda, and the precipitate (if any) washed with ether. The residue represents the amount of cinchonine. Finally, by distilling the ether from the washings can be ascertained the amount of amorphous alkaloid, which often, in the case of analysis of Indian barks, contains traces of quinamine.

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* A washing-bottle containing an excess of pure crystallized Herapathite in alcohol of 95 per cent. may be kept ready for application.

Prollius's Method for the Estimation of Total Alkaloids in Cinchona-bark, as modified by De Vrij.—The principle of the method referred to consists in using for the extraction of the alkaloids a mixture of 88 parts (by weight) of ether, 8 of alcohol (92 to 95 per cent.), and 4 of liquid ammonia. Prollius directs 10 grammes of this liquid to be taken for every gramme of bark; but De Vrij recommends the proportion of menstruum to be doubled. 10 grammes of finely-powdered bark are introduced into a well-closed bottle, and, after being carefully tared, 200 grammes of the ethereal liquid are added. The whole is now shaken at intervals during one hour (Biel says *four* hours), this length of time having been ascertained by comparative experiments to be sufficient. The bottle is then again weighed, and if evaporation has taken place the necessary quantity of ether mixture is added. As much as possible of the clear liquid is now poured off into a flask, and the bottle again weighed; the difference in weight gives the amount of solution taken. The ether is then recovered by distillation, and the residual liquid, containing alkaloid and waxy matter, is transferred to a tared porcelain dish and glass rod, the flask being washed with a little spirit. The evaporation is now continued on the water-bath until the weight is constant. This gives the amount of crude alkaloid. For instance, 10 grammes of succirubra-bark were digested with 200 grammes of ethereal liquid: 159.8 grammes of the clear solution gave a residue of 0.78 gramme, or 9.76 per cent. of crude alkaloid.

To estimate the pure alkaloids, the crude residue is dissolved in dilute hydrochloric acid, filtered, washed as long as the washings precipitate with solution of soda, and the whole made alkaline and shaken with chloroform. After standing twelve hours the clear chloroformic solution is run into a flask and evaporated by distillation. The residue is transferred with a little spirit to a tared dish and stirrer, and heated on the water-bath till the weight is constant. Particular attention should be paid to the latter point. In the instance referred to 0.648 gramme of alkaloid was obtained, equivalent to 8.11 per cent., or about 1½ per cent. less than the amount of crude alkaloid. By estimating the crude alkaloid and deducting 1½ per cent., a result will be arrived at, with loss of but little time, which, for the practical purposes of the pharmacist, will be sufficiently near the truth.

Carles's Process for the Valuation of Cinchona-barks.—An average sample of the bark is reduced to fine powder and passed through a sieve without residue. Twenty grammes are then taken and intimately mixed in a mortar with 8 grammes of slaked lime previously mixed with 35 grammes of water. This mixture, spread on a plate, is dried in the air in summer or on a water-bath at other times. When all the moisture has evaporated, the lumps are broken up and the powder packed in a percolator with a piece of lint at the bottom. Chloroform is then passed through in successive portions till the mass is exhausted. This is ascertained by receiving the last drops on a watch-glass, evaporating to dryness and pouring on the residue water acidulated with dilute sulphuric acid, then solution of chlorine, and lastly ammonia. When a green color is no longer produced it is known that all the quinine has been removed. When the operation is well conducted about 150 grammes of chloroform suffice for this purpose. The menstruum retained by the mass is displaced by water, and the whole of the chloroform solution is either distilled or evaporated to dryness. To separate the alkaloids from the residue it is treated several times in the cold with diluted sulphuric acid (1 to 10), 10 to 12 cubic centimetres being sufficient. This solution, thrown upon a moistened filter, passes through colorless and free from resinous matter. It is raised to the boiling-point and ammonia cautiously added, so as to leave the liquid with a *slightly acid* reaction. The sulphate of ammonium thus formed appears to prevent the mother-liquids from retaining sulphate of quinine in solution. All the quinine crystallizes out in the state of sulphate. After some time it is collected on a double filter, the mother-liquors displaced by a little water, and the crystals dried and weighed. It is preferable to dry completely at 100° C., and after weighing in this state to add the 12 per cent. of water which is lost by this treatment. The other alkaloids retained in the mother-liquors are separated by precipitation.

A quantitative determination of the purity of commercial sulphate of quinine may be made by dissolving 1 gramme of the salt in 20 grammes of alcohol containing .7562 per cent. of sulphuric acid, adding 20 more grammes of alcohol, and precipitating the quinine as Herapathite in the manner above described. If pure, one gramme of quinine should yield 1.3 grammes of Herapathite (De Vrij).

Kerner's Test for the Purity of Sulphate of Quinine.—This has already been described as a qualitative test under Quinine (p. 386). It may be applied quantitatively in the following manner: 5 grammes of the sulphate to be tested are triturated in a mortar with a little cold water, and the whole placed in a stoppered bottle previously calibrated for 50 c.c. Water is added to 50 c.c., and the mixture is well agitated and set aside for a day or so. It is then filtered, and a portion of the filtrate, say 30 c.c., is examined. To 30 c.c. of the filtrate 42 c.c. of ammonia solution (sp. gr. 0.96) are added, and the mixture agitated. If a permanent precipitate remains it is collected on a filter, washed, dried at 100° C., and weighed. This weight is the amount of alkaloid other than quinine in 3 grammes of sulphate. Multiplied by 33.3, it is the percentage of alkaloid other than quinine, generally cinchonidine, contained in the specimen of sulphate. To obtain the amount of sulphate of cinchonidine corresponding to this percentage it must be multiplied by 1.217.

Paul's Modification of Kerner's Test for Sulphate of Cinchonidine in Sulphate of Quinine.—Dissolve 4 or 5 grammes of the salt in 80 to 150 c.c. of boiling water. Set aside for some hours or during a night. Most of the quinine sulphate is deposited, while the more soluble cinchonidine sulphate remains in solution. Filter. To the filtrate in a bottle add ether, shaking occasionally, until a distinct layer of ether remains undissolved. Add now ammonia in excess; quinine is precipitated, and then redissolved by the excess of ammonia, while cinchonidine remains insoluble. Set this mixture aside for a few hours; any cinchonidine which may have been carried into solution in the ether along with the quinine will separate out in a crystalline state. If a weighed quantity of the original salt has been operated on, the separated cinchonidine may be collected on a filter, washed with a little ether, and weighed. Care must be taken that the filter does not retain quinine deposited by the evaporating of the ether which held it in solution.

This will be avoided if the flask in which the operation is conducted is of such a size that the ethereal solution of quinine collects in the neck; for the latter liquid may be removed by a pipette, a little more ether then poured in, the cork replaced, and the whole shaken and set aside; and this operation repeated two or three times before the cinchonidine is collected. The cinchonidine, being thus washed with a minimum of ether, suffers a minimum loss.

The quinine sulphate deposited from the first aqueous solution should be again recrystallized and its mother-liquor treated as above; and even the sulphate deposited in this second treatment should be once more carried through the operation. The whole of the cinchonidine may finally be collected on one filter.

The aqueous filtrates may even be evaporated, set aside, filtered, and the ether test again applied (Parker).

Sulphate of quinine normally contains 14.45 per cent. of water; sulphate of cinchonidine, 13.17 per cent.—all given off at 100° to 115° C. The drying should therefore be effected at 100° C., and the dried salt weighed in well-fitting weighing-tubes. 100 parts of cinchonidine are equivalent to 116 parts of sulphate of cinchonidine.

Sulphate of cinchonidine is almost the only salt likely to be accidentally present in the sulphate of quinine of trade, much quinidine being rarely present in bark, and sulphate of cinchonine being sufficiently soluble to always remain in the mother-liquors of sulphate of quinine. The sulphate of cinchonidine may vary from 1 to 12 per cent., but more usually is present to the extent of about 6 per cent.

Quinina, U. S. P.: "If 1 gm. of quinine be mixed, in a mortar, with 0.5 gm. of sulphate of ammonium and 5 c.c. of distilled water, the mixture thoroughly dried on the water-bath, the residue (which should be neutral to test-paper) agitated with 10 c.c. of distilled water, this mixture macerated at 15° C. (59° F.) for half an hour, then filtered through a small filter, 5 c.c. of the filtrate taken in a test-tube, and 7 c.c. of water of ammonia (sp. gr. 0.960) then added,—on closing the test-tube with the finger and gently turning it until the ammonia is fully intermixed, a clear liquid should be obtained. If the temperature of maceration has been 16° C. (60.8° F.), 7.5 c c. of the water of ammonia may be added; if 17° C. (62.6° F.), 8 c c. may be added. In each instance a clear liquid indicates the absence of more than about 1 per cent. of cinchonidine and quinidine, and of more than traces of cinchonine."

Quininæ Sulphas, U. S. P.: "If 1 gm. of the salt be placed in a porcelain capsule, and dried at a temperature of 100° C. (212° F.) for three hours, or until a constant weight is attained, the remainder, cooled in a desiccator, should weigh not less than 0.838 gm. (abs. of more than 8 molecules, or 16.18 per cent., of water). If the residue thus dried at 100° C. (212° F.) be agitated with 10 c.c. of distilled water, the mixture macerated at 15° C. (59° F.) for half an hour, then filtered through a small filter, 5 c.c. of the filtrate taken in a test-tube, and 7 c.c. of water of ammonia (sp. gr. 0.960) then added,—upon treating this liquid as described above for *Quinina* the results there given should be obtained."

Of the Citrate of Iron and Quinine (*Ferri et Quininæ Citras*, B. P. and U. S. P.) it is officially stated that "50 grains dissolved in a fluidounce of water and treated with a slight excess of ammonia give a white precipitate, which, when collected on a filter, washed, and dried (at 260° F.), weighs 8 grains. The precipitate is almost entirely soluble in two or three fluidrachms of pure ether," and the ethereal solution set aside for twelve hours in a small well-corked bottle yields no crystalline deposit (of quinidine).

Another Process for the Determination of the Quinine of the Scaled Compound.—A weighed quantity of the scale, about 4 grammes, is dissolved in about 50 c.c. of water, and the whole is placed in a closed separating-funnel. About the same volume of chloroform is added, and enough ammonia to impart a distinctly alkaline reaction. The whole is well agitated, and is allowed to stand until the two layers separate. The chloroformic layer is then run into a weighed dish. The aqueous solution is treated in this way with two more portions of chloroform, about 25 c.c. each. The mixed chloroformic solutions are then evaporated to dryness over a water-bath, and the weight of the residue determined. To the residue is added about 25 c. c. of water and enough dilute sulphuric acid to impart a decidedly acid reaction. The mixture is next heated over a water-bath until, the solution remaining acid, the residue has completely dissolved. Dilute soda solution is afterward added with great care until the solution is exactly neutral. The dish is then removed, and the solution allowed to cool and rest over night, when the quinine will have separated in crystals of ordinary sulphate. These should be collected on a filter, and the mother-liquor tested with litmus-paper. If it is acid, it must be warmed over a water-bath, and dilute soda solution added to exact neutralization, and the solution set aside as before, when some more crystals will probably separate. These are also collected, and with the former ones washed, dried at 100° C., and weighed [$(C_{20}H_{24}N_2O_2)_2,H_2SO_4 = 746$]. To this weight must be added 1 gramme for every 750 c.c. of mother-liquor for quinine sulphate which it retains. From this weight of anhydrous quinine sulphate is calculated its equivalent of hydrous quinine $(C_{20}H_{24}N_2O_2)_2,2H_2O = 684$, the approximate formula of hydrous quinine dried over a water-bath. The weight thus obtained is compared with the weight of total alkaloid determined, both having been reduced to percentages. The amount of hydrous quinine calculated from the crystals of sulphate should not be much below that weighed directly. In good specimens the difference will be about 1 per cent. (See also a paper by Fletcher in the *Pharmaceutical Journal* for Sept. 20, 1879; also in that for Sept. 18, 1880, by De Vrij.)

MORPHINE OR MORPHIA.

The official (U. S. P.) *process for the assay of opium* is conducted in the following manner:—

	Grammes.
Opium, in any condition to be valued, ...	7
Lime, freshly slaked, ...	3
Chloride of Ammonium, ...	3
Alcohol,	
Stronger Ether,	
Distilled Water, each a sufficient quantity.	

"Triturate together the opium, lime, and 20 c.c. of distilled water in a mortar until a uniform mixture results; then add 50 c.c. of distilled water, and stir occasionally during half an hour. Filter the mixture through a plaited filter three to three and one-half inches (75 to 90 millimetres) in diameter into a wide-mouthed bottle or stoppered flask (having the capacity of about 120 c.c. and marked at exactly 50 c.c.), until the filtrate reaches this mark. To the filtered liquid (representing 5 grammes of opium) add 5 c.c. of alcohol and 25 c.c. of stronger ether, and shake the mixture; then add the chloride of ammonium, shake well and frequently during half an hour, and set it aside for twelve hours. Counterbalance two small filters; place one within the other in a small funnel, and decant the ethereal layer as completely as practicable upon the filter. Add 10 c.c. of stronger ether to the contents of the bottle and rotate it; again decant the ethereal layer upon the filter, and afterward wash the latter with 5 c.c. of stronger ether, added slowly and in portions. Now let the filter dry in the air, and pour upon it the liquid in the bottle, in portions, in such a way as to transfer the greater portion of the crystals to the filter. Wash the bottle, and transfer the remaining crystals to the filter, with several small portions of distilled water, using not much more than 10 c.c. in all, and distributing the portions evenly upon the filter. Allow the filter to drain, and dry it, first by pressing it between sheets of bibulous paper, and afterward at a temperature between 55° and 60° C. (131° to 140° F.). Weigh the crystals in the inner filter, counterbalancing by the outer filter. The weight of the crystals in grammes, multiplied by *twenty*, equals the percentage of morphine in the opium taken."

"On exhausting 100 parts of opium, previously dried at a temperature of 105° C. (221° F.), with cold water, and evaporating the solution to dryness, an extract is obtained which should weigh between 55 and 60 parts."—U. S. P.

Prollius's Method for the Determination of Morphine in Opium.—5 to 10 grammes of opium are weighed and extracted with 100 c.c. of 34-per cent. spirit. The resulting tincture is well shaken with 50 c.c. of ether and 2 c.c. of solution of ammonia in a stoppered bottle, and then allowed to stand from twelve to twenty-four hours. The liquids separate slowly, and retain, partly in the ether and partly in the alcoholic liquid, the coloring-matter, narcotine, and other crystallizable constituents of opium, while the morphine separates in crystals between the two layers, and finally sinks to the bottom. The fluid portion is decanted, the crystals are washed with diluted alcohol dried at 100° C., and weighed.

Petit's Method.—Take 15 grammes of opium, suspend it in 75 grammes of water, and afterward throw it upon a filter. Take 55 grammes of the filtrate, which represents 10 grammes of opium, add 3 c.c. of ammonia solution, and agitate. The morphine deposits rapidly in the form of a crystalline powder. The whole is allowed to stand for a quarter of an hour, and then 27 grammes of alcohol (of 95 per cent.) are added; after shaking several times it is again allowed to stand for half an hour, and then thrown upon a tared filter. The alkaloid is washed upon the filter with 50 per cent. alcohol. It is then dried at 100° C. and weighed.

Flückiger's Method.—Take of powdered opium 8 grammes, cold water 80 grammes; shake the mixture frequently; after twelve hours filter. The filter should have a diameter of 5 inches. The operation will afford on an average 65 to 70 grammes of clear liquid. No washing is to take place. 42.5 grammes of the liquid are collected in a little phial, the weight of which has previously been noted. Next add to the solution 12 grammes of alcohol (sp. gr. 0.812–0.815), 10 grammes of ether, and 1.5 grammes of ammonia-water of 0.960 sp. gr. The mixture after shaking will remain clear, and a colorless layer of ether will appear on its surface. The phial is corked and allowed to stand without further shaking. After an hour or two crystals of morphine begin to be formed, mostly at the junction of the two layers. Presently they sink to the bottom, and after a day or two the whole amount of whitish or white crystals of the alkaloid will have been deposited. They are then to be collected by using two folded filters having a diameter of four inches. The phial is rinsed out with a mixture of 6 grammes of alcohol and 5 grammes of ether, and lastly with 10 grammes of ether, these liquids being gradually poured on to the crystals in order to wash them. The funnel in the mean time is carefully covered. The crystals are subsequently cautiously pressed between the folds of the two filters, which will almost completely absorb the mother-liquor which the crystals of morphine may still retain. It will now be quite easy to remove the alkaloid neatly from the filter; it must be weighed in the phial, in which some crystals may have remained obstinately attached to the walls. The phial and contents, dried at 100° C., contain the whole amount of morphine precipitated in the hydrous condition—namely, $C_{17}H_{19}NO_3 + H_2O$. The operator finally ascertains the purity of the crystals. To this end he takes 1 decigramme of the morphine and dissolves it in 10 grammes of lime-water. If the lime-water be duly saturated in the cold, the quantity mentioned will be a little more than sufficient. The morphine will probably leave only a very trifling amount of coloring-matter, quite insufficient to influence appreciably the percentage of alkaloid. Should narcotine be present it will remain undissolved. It is important to precipitate the morphine from a solution containing alcohol and ether. By adding ammonia to an aqueous solution a flocculent matter is precipitated. This abundant amorphous mass—an alkaloid or not, it is certainly far from being morphine—remains in solution if the liquid contains a little alcohol, one-third alcohol of the volume of the aqueous filtrate being quite sufficient for the purpose. Of no less importance is the action of the ether. It not only prevents the narcotine from being thrown down together with the morphine, but ether promotes the formation of distinct and pure crystals of morphine, this alkaloid separating very readily from a liquid saturated with ether. E. R. Squibb has published useful details respecting this process.

Mylius's Method.—For the colorimetric assay of morphine in opium by means of iodic acid see *New Remedies* for June, 1881.

SUGAR.

The qualitative test of sugar by means of an alkaline copper solution (*vide* p. 411) may be applied in the estimation of sugar in sacchariferous substances.

Process.—34.65 grammes of pure dry crystals of ordinary sulphate of copper are dissolved in about 250 c.c. of distilled water, and 173 grammes of pure crystals of the double tartrate of potassium and sodium are dissolved in 480 c.c. of solution of caustic soda of sp. gr. 1.14. The solutions are mixed, and water added until 1 litre of solution is obtained. 100 c.c. of this solution represent 3.464 grammes of sulphate of copper, and correspond to 0.5 of a gramme of pure anhydrous grape-sugar, 0.475 of cane-sugar, 0.82 of maltose, or 0.45 of starch. It must be preserved in a well-stoppered bottle to prevent absorption of carbonic acid, and be kept in a dark place. Should it give a precipitate on boiling, a little solution of soda may be added when making experiments. A solution of this strength is officially (U. S. P.) termed "Test-Solution of Potassio-cupric Tartrate," or "Fehling's Solution."

Dissolve 0.475 of pure dry powdered cane-sugar in about 50 c.c. of water, convert into grape-sugar by acidulating with sulphuric acid and boiling for an hour or two, make slightly alkaline with carbonate of sodium, and dilute to 100 c.c. Place 10 c.c. of the copper solution in a small flask, dilute with three or four times its bulk of water, and gently boil. Into the boiling liquid drop the solution of sugar from a burette, one cubic centimetre or less at a time, until, after standing for the precipitate to subside, the supernatant liquid has just lost its blue color; 10 c.c. of the solution of the sugar should be required to produce this effect = 0.0475 of cane-sugar, 0.082 of maltose, or 0.05 of grape-sugar. Experiments on pure cane-sugar must be practised until accuracy is attained; syrups, diabetic urine, and saccharated substances containing unknown quantities of sugar may then be analyzed.

Starch is converted into grape-sugar by gentle ebullition with dilute acid for eight or ten hours, the solution being finally diluted so that one part of starch, or rather sugar, shall be contained in about 150 of water.

Saccharimetry.—A generic term for certain volumetric operations undertaken with the view of ascertaining the quantity of sugar present in any matter in which it may be contained.

Saccharimetry is frequently performed upon common syrup

(*Syrupus*, B. P.) and solutions which are known to contain nothing but cane- (ordinary) sugar, the object being merely to ascertain the amount present. In such a case it is only necessary to take the specific gravity of the liquid at 60° F., and then refer to a previously prepared Table of density and percentages :—

Specific gravity.	Sugar, per cent.	Specific gravity.	Sugar, per cent.	Specific gravity.	Sugar, per cent.
1.007	1.8	1.100	23.7	1.210	46.2
1.014	3.5	1.108	25.6	1.221	48.1
1.022	5.2	1.116	27.6	1.231	50.0
1.029	7.0	1.125	29.4	1.242	52.1
1.036	8.4	1.134	31.5	1.252	54.1
1.044	10.4	1.143	33.4	1.261	56.0
1.052	12.4	1.152	35.2	1.275	58.0
1.060	14.4	1.161	37.0	1.286	60.1
1.067	16.3	1.171	38.8	1.289	62.2
1.075	18.2	1.180	40.6	1.309	64.4
1.083	20.0	1.190	42.4	1.321	66.6?
1.091	21.8	1.199	44.3	1.330 (B. P.)	66.6?

The sp. gr. may be taken by a hydrometer, technically termed a *saccharometer*. (The above spec. gravs. = 1° to 35° Baumé.)

If a liquid contains other substances besides cane-sugar, the test of specific gravity is of little or no value. Advantage may then be taken of the fact that syrup causes right-handed twisting of a ray of polarized light to an extent exactly proportionate to the amount of sugar in solution. The saccharine fluid is placed in a long tube having opaque sides and transparent ends, and a ray of homogeneous light, polarized by reflection from a black-glass mirror or otherwise, is sent through the liquid and optically examined by a plate of tourmaline, Nicol's prism, or other polarizing eye-piece. Attached to the eye-piece is a short arm which traverses a circle divided into degrees. The eye-piece and arm are previously so adjusted that when the ray is no longer visible the arm points to the zero of the scale of degrees. The saccharine solution, however, so twists the ray as to again render it visible ; and the number of degrees which the eye-piece has to be rotated before the ray is once more invisible is exactly proportionate to the strength of the solution. The value of the degrees having been ascertained by direct experiment and the results tabulated, a reference to the Table at once indicates the percentage of sugar in the liquid under examination. Grape-sugar also possesses the property of dextro-rotation, but less powerfully than cane-sugar; moreover, the former variety does not, like cane-sugar, suffer inversion of the direction of rotation on the addition of hydrochloric acid to its solution—an operation that furnishes data for ascertaining the amounts of cane- and of grape-sugar, or of crystallizable and non-crystallizable sugar, present in a mixture. In using the polariscope-saccharometer it is convenient to employ tubes of uniform size and always to operate at the same temperature. Various modes are adopted of applying, for the purposes of quantitative analysis, the action of syrup on polarized light.

ALCOHOL.

Mulder's process for the determination of the amount of alcohol in wines, beer, tinctures, and other alcoholic liquids containing vegetable matter is as follows:—Take the specific gravity and temperature of the liquid, and measure off a certain quantity (100 cubic centimetres); evaporate to one half or less, avoiding ebullition in order that particles of the material may not be carried away by the steam. Dilute with water to the original bulk, and take the specific gravity at the same temperature as before. Of the figures representing this latter specific gravity, all over 1.000 show to what extent dissolved solid matter affected the original specific gravity of the liquid. Thus, the specific gravity of a sample of wine at 15°.5 C. is 0.9951; evaporated till all alcohol is removed and diluted with water to the original bulk, the specific gravity at 15°.5 C. is 1.0081; 0.0081 represents the gravitating effect of dissolved solid matter in 0.9951 parts of original wine. 0.0081 subtracted from 0.9951 leaves 0.987, which is the specific gravity of the water and alcohol of the wine. Or divide the sp. gr. of the wine by the sp. gr. of the wine minus alcohol, carrying out the sum to four places of decimals; the quotient shows the sp. gr. of the water and alcohol only of the wine. On referring to a Table of the strengths of diluted alcohol of different specific gravities (p. 659), 0.987 at 15°.5 C. is found to indicate a spirit containing 8 per cent. of real alcohol. Mulder's process is that adopted officially (U. S. P.) for ascertaining the strength of white wine (*Vinum Album*) and red wine (*Vinum Rubrum*). If the foregoing operation be conducted in a retort, the liquid being boiled and the steam carefully condensed, the distillate, diluted with water to the original bulk of wine operated on, will still more accurately represent the amount of water and alcohol in the wine, its specific gravity showing the percentage of real alcohol present.

DIALYSIS.

Dialysis (from διὰ, *dia*, through, and λύσις, *lusis*, a loosing or resolving) is a term applied by Graham to a process of analysis by diffusion through a septum. The apparatus used in the process is called a *dialyzer*, and is constructed and employed in the following manner. The most convenient septum is the commercial article known as *parchment-paper*, made by immersing unsized paper for a short time in sulphuric acid ; it is sold by most dealers in chemical apparatus. A piece of this material is stretched over a gutta-percha hoop and secured by a second external hoop. Dialyzers of useful size are one or two inches deep and five to ten inches wide. Liquids to be dialyzed are poured into the dialyzer, which is then floated in a flat dish containing distilled water. The portion passing through the septum is termed the *diffusate* ; the portion which does not pass through is termed the *dialysate.*

The practical value of dialysis depends upon the fact that certain substances will diffuse through a given septum far more readily than others. Uncrystallizable bodies diffuse very slowly. Of such matters as starch, gum, albumen, and gelatin, the last named is perhaps least diffusive ; hence substances of this class are termed *colloids*, or bodies like *collin*, which is the soluble form of gelatin. Substances which diffuse rapidly are most crystalline ; hence bodies of this class are termed *crystalloids.*

Solution of two parts of the following-named substances in 100 parts of distilled water were dialyzed by Graham for twenty-four hours. The amounts of each substance which passed through the septum bore the following relations to one another :—

Chloride of sodium	1000
Ammonium	847
Theine	703
Salicin	503
Cane-sugar	472
Amygdalin	311
Extract of logwood	168
Catechu	159
Extract of cochineal	51
Gallo-tannic acid	30
Extract of litmus	19
Purified caramel	5

Ten per cent. solutions, under similar circumstances, gave the following results:—

Gum-arabic	4
Starch-sugar	266
Cane-sugar	214
Glycerin	440
Alcohol	476
Chloride of sodium	1000

Dialyzed iron, an aqueous solution of about 5 per cent. of highly basic oxychloride of iron, is obtained by saturating solution of perchloride of iron with ferric hydrate, by adding ammonia, or, better, carbonate of sodium, and shaking vigorously until the precipitated hydrate ceases to redissolve, filtering if necessary, placing on a dialyzer floating in distilled water, and displacing the fluid in the dish by water daily for a week or two, or until the diffusate gives no reaction with nitrate of silver. The crystalloids (chloride of sodium or other salt) pass through the dialyzer; the colloid fluid which does not pass through the dialyzer is the highly basic oxychloride of iron, or so-called "dialyzed iron" or "dialytic iron." This fluid has very little taste of iron. Its value as a medicine has been questioned, its non-diffusibility suggesting that it never passes out of the intestinal canal, and therefore never gets into the blood. It is sometimes prepared by dissolving in solution of ferric chloride as much ferric hydrate as it will take up, with frequent shaking, during three or four weeks.

The phenomena of dialysis show that crystalloids are superior to colloids in affinity for water. If a solution of chloride of sodium be placed at the bottom of a jar and covered by a hot solution of gelatin of sufficient strength to solidify on cooling, the chloride of sodium will diffuse up into the solid jelly, because the water of the solid jelly has a greater affinity for the salt than it has for the gelatin. The solid jelly may obviously be reduced in thickness, and saline liquids placed above it; indeed the conditions would then be still more favorable for diffusion. Replace the stratum of jelly by a permanent colloid, such as parchment-paper; the result is the same, but the permanent character of the septum admits of its practical application.

Further researches on dialysis will probably throw much light on several important points in connection with physiological chemistry; for there is little doubt that alimentary matter passes through the cell-walls of animals and plants by this process.

QUESTIONS AND EXERCISES.

1055. Carbonate of potassium is said to lose 16 per cent. of water on exposure to a red heat; give the details of manipulation observed in verifying this statement.

1056. Write a few paragraphs descriptive of the process of ultimate organic analysis.

1057. In what forms are carbon, hydrogen, and nitrogen weighed in quantitative analysis?

1058. In the combustion of .41 of a gramme of sugar, what weights of products will be obtained? *Ans.* .632 of carbonic acid gas (CO_2) and .237 of water (H_2O).

1059. How is cinchona assayed for mixed alkaloids?

1060. On what facts does De Vrij found his method for the separation and quantitative determination of all the cinchona alkaloids?

1061. Describe De Vrij's process for the assay of commercial sulphate of quinine.

1062. Give the official method for the estimation of morphine in opium.

1063. Mention the operation necessary for the estimation of the proportion of sugar in saccharated carbonate of iron or in a specimen of diabetic urine.

1064. What is understood by *Saccharimetry?*

1065. Give two processes for the estimation of the percentage of alcohol in tinctures, wines, or beer.

1066. Define dialysis.

CONCLUSION.

Detailed instructions for the quantitative analysis of potable water, articles of food, general technical products, special minerals, soils, manures, air, illuminating agents (including solid fats, oils, spirits, petroleum, and gas), dyes, and tanning-materials would scarcely be in place in this volume.

The course through which the reader has been conducted will, it is hoped, have taught the principles of the science of Chemistry, and given special knowledge concerning the applications of that science to medicine and pharmacy, as well as have imparted sufficient manipulative skill to meet the requirements of manufacture or analysis. The author would venture to suggest that this knowledge be utilized, not only in the way of personal advantage, but in experimental researches on chemical subjects connected with therapeutics and pharmacy. The discovery and publication of a new truth, great or small, is the best means whereby to aid in advancing the calling in which we may be engaged, benefit our fellow-creatures and ourselves, and contribute to that "ultimate end of knowledge" which Bacon defined as "the glory of the Creator and the endowment of human life."

APPENDIX.

TABLE OF TESTS FOR IMPURITIES IN PREPARATIONS OF THE UNITED STATES PHARMACOPŒIA.*

Name of Preparation.	Impurities.	Tests.	Page.
Acaciæ Gummi,	Starch.	Iodine.	271
Acidum Aceticum,	Copper, Lead, or Tin.	Sulphuretted Hydrogen.	254
	Iron.	Excess of Ammonia.	157
	Calcium.	Oxalate of Ammonium.	113
	Other mineral matter.	Evaporation and ignition.	100
	Empyreumatic substances.	Color and odor with Potash.	92
		Reduction by Permanganate of Potassium.	92
	Organic matter.	Sulphuric Acid.	320
	Nitric Acid.	Sulphuric Acid and Sulphate of Iron.	286
	Sulphuric Acid.	Chloride of Barium.	307
	Hydrochloric Acid.	Nitrate of Silver.	264
	Sulphurous Acid.	Nascent Hydrogen.	304
		Nitrate of Silver.	304
Acid. Acetic. Glaciale,	Sulphurous Acid.	Nascent Hydrogen, or Nitrate of Silver.	304
Acidum Boricum,	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Hydrochloric Acid.	Nitrate of Silver and Nitric Acid.	264
	Lead, Copper, Iron, etc.	Sulphide of Ammonium.	157
	Calcium.	Oxalate of Ammonium.	113
	Sodium Salts.	In flame on Pt. wire.	87
Acidum Benzoicum,	Chlorobenzoic Acid.	Cupric Oxide and flame-test.	190
	Cinnamic Acid.	Permanganate of Potassium and water.	334
	Other organic matter.	Odor; warm Sulphuric Acid.	334
Acidum Carbolicum,	Creasote and Cresylic Acid.	Glycerin, and dilution, oxidation, etc.	449
Acidum Chromicum,	More than trace of Sulphuric Acid.	Chloride of Barium.	307

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* The manipulations necessary to be observed in testing for impurities will be found described in the paragraphs treating of those substances. The Table also includes references to processes for ascertaining deficiency in strength of official articles.

The other characters and tests of pharmacopœial chemical compounds have been given in connection with the respective synthetical and analytical reactions.

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Acidum Citricum,	Tartaric and Oxalic Acids.	Acetate of Potassium and Alcohol.	319
	Tartaric Acid.	Bichromate of Potassium.	324
	Lead or Copper.	Sulphuretted Hydrogen.	218
	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Mineral matter.	Incineration.	100
Acidum Gallicum,	Tannic Acid.	Gelatin, Alkaloidal Salts, Tartarated Ant'ny, etc.	354
Acidum Hydrobromic. Dilut.,	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
Acidum Hydrochloricum,	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Sulphurous Acid.	Nascent Hydrogen.	304
	Arsenic.	Sulphuretted Hydrogen: Copper.	169
	Lead, Iron, or Copper.	Sulphydrate of Ammonium.	157
	Free Chlorine.	Iodide of Potassium.	271
Acid. Hydrocyanicum, Dil.,	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Hydrochloric Acid.	Ppt. by Nitrate of Silver; insol. in Nitric Acid.	264
Acidum Lacticum,	Hydrochloric Acid.	Nitrate of Silver.	264
	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Sarcolactic Acid.	Sulphate of Copper.	345
	Lead or Iron.	Ammonia and Sulphydrate of Ammonium.	157
	Sugars.	Potassio-cupric Tartrate.	630
	Glycerin.	Hydrate of Zinc and Absolute Alcohol.	455
	Other organic matter.	Cold Sulphuric Acid.	334
Acidum Nitricum,	Iron or Lead.	Ammonia and Sulphydrate of Ammonium.	157
	Copper.	Excess of Ammonia.	189
	Mineral matter.	Evaporation and gentle ignition.	100
	Arsenic Acid.	Excess of Potash, boil with Zinc.	171
	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Hydrochloric Acid.	Nitrate of Silver.	264
	Free Iodine.	Mucilage of Starch.	271
	Iodic Acid.	Starch and Sulphuretted Hydrogen.	293
Acidum Oleicum,	Palmitic and Stearic Acids.	Saponification. Acetic Acid, and Acetate of Lead.	463
	Fixed Oils.	Alcohol.	463
Acidum Phosphoricum.	Phosphorous Acid.	Nitrate of Silver; Mercuric Chloride.	342
	Arsenic Acid.	Sulphuretted Hydrogen.	173

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Acidum Phosphoricum,	Nitric Acid.	Sulphuric Acid and Ferrous Sulphate.	286
	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Hydrochloric Acid.	Nitrate of Silver and Nitric Acid.	264
	Pyro- or Meta-phosphoric Acid.	Tincture of Chloride of Iron, Albumen.	347
Acidum Salicylicum,	Hydrochloric Acid.	Nitrate of Silver and Nitric Acid.	264
	Organic matter and Iron.	Crystallization from Alcohol (white).	
	Organic matter.	Cold Sulphuric Acid.	334
	Carbolic Acid.	Chlorate of Potassium, Hydrochloric Acid, and Ammonia.	451
Acidum Sulphuricum,	Lead.	Alcohol.	211
	Nitric Acid.	Solution of Ferrous Sulphate.	286
	Hydrochloric Acid.	Sulphate of Silver.	265
	Lead, Arsenic, or Copper.	Sulphuretted Hydrogen.	218
	Iron.	Excess of Ammonia.	157
	Mineral matter.	Incineration.	100
	Arsenious or Sulphurous Acid.	Nascent Hydrogen.	171
Acidum Sulphurosum,	Much Sulphuric Acid.	Chloride of Barium.	307
Acidum Tannicum,	Mineral matter.	Incineration.	100
Acidum Tartaricum,	Lead or Copper.	Sulphuretted Hydrogen.	218
	Iron.	Ammonia and Sulphydrate of Ammonium.	151
	Sulphuric Acid.	Chloride of Barium.	307
	Mineral matter (more than trace).	Incineration.	100
Adeps,	Alkalies.	Litmus.	94
	Starch (flour).	Iodine.	271
	Chloride (of Sodium).	Nitrate of Silver.	264
	Excess of water.	Drying on water-bath.	610
Æther,	Mineral matter.	Evaporation. (See also Æther Fortior.)	100
Æther Aceticus,	Mineral matter.	Evaporation.	100
	Acetic Acid.	Test-papers.	94
	Water.	Specific gravity.	436
	Alcohol.	Boiling-point.	436
Æther Fortior,	Acid.	Test-papers.	94
	Excess of water and Alcohol.	Agitation with Glycerin; boiling-point.	434
Alcohol,	Fusel Oil.	Water and Glycerin.	429
	Amylic Alcohol.	Sulphuric Acid.	430
	Methyl Alcohol. Aldehyd and Oak Tannin.	Solution of Potash.	430

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Alcohol,	Methyl Alcohol.	Carbonate of Lead and Permanganate.	430
	Fixed residue or resin.	Evaporation.	100
Alcohol Absolutum,	Water.	Sulphate of Copper (anhydrous).	188
Alumen,	Ammonia Alum.	Potash or Soda.	96
	Zinc or Lead.	Sulphydrate of Ammonium in alkaline filtrate.	133
	More than trace of Iron.	Ferrocyanide of Potassium.	157
Aluminii Hydras,	Iron.	Ferrocyanide of Potassium.	157
	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Zinc or Lead.	Sulphydrate of Ammonium.	133
	Alkaline Salts (more than trace).	Solution in water and evaporation.	100
Aluminii Sulphas,	Iron.	Ferrocyanide of Potassium.	157
Ammonii Benzoas,	Fixed Salts.	Incineration. (See also Acidum Benzoicum.)	100
Ammonii Bromidum,	Bromate (of Ammonium).	Diluted Sulphuric Acid.	268
	Iodide (of Ammonium).	Chlorine-water and mucilage of Starch.	271
	Sulphate (of Ammonium).	Chloride or Nitrate of Barium.	307
	More than 3 per cent. of Chloride.	Quantitative Analysis.	569
Ammonii Carbonas,	Sulphate (of Ammonium).	Chloride or Nitrate of Barium.	307
	Chloride (of Ammonium).	Nitrate of Silver.	264
	Metals.	Sulphuretted Hydrogen.	218
	Empyreumatic substances.	Excess of Sulphuric Acid and Permanganate.	92
Ammonii Chloridum,	Barium.	Sulphuric Acid.	102
	Metals.	Sulphuretted Hydrogen or Sulphydrate of Ammonium.	218
	Sulphate (of Ammonium).	Nitrate of Barium.	307
	Iron.	Ferrocyanide of Potassium.	157
Ammonii Iodidum,	Sulphate (of Ammonium).	Chloride or Nitrate of Barium.	307
	Chloride and Bromide (excessive).	Ammoniacal solution, Nitrate of Silver, and Nitric Acid; and Quantitative Analysis.	271
	Iron.	Ferrocyanide of Potassium.	157

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Ammonii Iodidum,	Free Iodine.	Mucilage of Starch.	271
Ammonii Nitras,	Sulphate (of Ammonium).	Chloride or Nitrate of Barium.	307
	Chloride (of Ammonium).	Nitrate of Silver.	264
Ammonii Phosphas,	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Sulphate (of Ammonium).	Chloride or Nitrate of Barium.	307
	Chloride (of Ammonium).	Nitrate of Silver.	264
Ammonii Sulphas,	Lead or Iron.	Sulphide of Ammonium.	218
	Chloride (of Ammonium).	Nitrate of Silver.	264
Ammonii Valerianas,	Acetate (of Ammonium).	Ferric Chloride.	297
	Sulphate (of Ammonium).	Nitrate or Chloride of Barium.	307
	Chloride (of Ammonium).	Nitrate of Silver.	264
Amyl Nitras,	Excess of free acid.	Quantitative Analysis.	563
Antimonii et Potassii Tartras,	Sulphate (of Potassium).	Chloride of Barium.	307
	Chloride (of Potassium).	Nitrate of Silver.	264
	Iron and other metals.	Ferrocyanide of Potassium and Acetic Acid.	157
	Calcium.	Oxalate of Ammonium.	113
	Arsenic.	Nascent Hydrogen and Nitrate of Silver.	171
Antimonii Oxidum,	Same as Ant. et Pot. Tart., *q. v.*		
Antimonii Sulphidum Purif.,	Metallic Sulphides.	Ignition with Nitrate of Soda.	174
	Arsenic.	Ammonio-nitrate of Silver.	174
Antimonium Sulphuratum,	Sulphate (of Sodium).	Chloride or Nitrate of Barium.	307
Aqua,	Metallic impurities.	Sulphydrate of Ammonium.	218
	Organic matter.	Permanganate of Potassium.	126
Aqua Ammoniæ,	Empyreumatic substances.	Neutralization with Sulphuric Acid and odor; also Permanganate.	92
	Carbonate.	Lime-water.	311
	Sulphate.	Chloride or Nitrate of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Metals.	Sulphuretted Hydrogen.	218
	Calcium.	Oxalate of Ammonium.	113
Aqua Aurantii Florum,	Metals (Pb, Cu, Sn).	Sulphuretted Hydrogen.	218

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Aqua Destillata,	Metals.	Sulphuretted Hydrogen or Sulphydrate of Ammonium.	218
	Sulphuric radical.	Chloride or Nitrate of Barium.	307
	Hydrochloric radical.	Nitrate of Silver.	264
	Calcium.	Oxalate of Ammonium.	113
	Ammonia or its salts.	Mercuric Chloride and Carbonate of Potassium, or Nessler's Reagent.	558
	Organic matter.	Permanganate of Potassium.	126
Argenti Iodidum,	Chloride (of Silver).	Boil with Carbonate of Ammonium, and add Nitric Acid.	265
Argenti Nitras,	Metallic impurities.	Hydrochloric Acid and evaporation.	265
Argenti Oxidum,	Carbonate.	Acid (Hydrochloric).	311
Atropina,	Mineral matter.	Incineration.	100
Atropinæ Sulphas,	Mineral matter.	Incineration.	100
Auri et Sodii Chloridum,	Free Acid.	Ammonia fumes.	97
Aurum,	Copper or Silver.	Nitric Acid.	242
Balsamum Peruvianum,	Volatile Oil.	Distillation with water.	469
	Gurjun Balsam.	Bisulphide of Carbon.	480
Benzinum,	Heavy Hydrocarbons.	Evaporation at low temp., and odor.	448
	Pyrogenous products and Sulphur compounds.	Spirit of Ammonia and Nitrate of Silver.	448
	Benzol.	Sulphuric and Nitric Acids.	448
Bismuthi Citras,	Nitrate.	Sulphuric Acid and Ferrous Sulphate.	286
Bismuth. et Ammon. Cit.,	Nitrate.	Sulphuric Acid and Ferrous Sulphate.	286
Bismuthi Subcarbonas,	Insoluble salts.	Dilute Nitric Acid.	372
	Lead.	Sulphuric Acid.	211
	Copper.	Excess of Ammonia.	189
	Silver.	Hydrochloric Acid.	264
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Alkalies and alk. earths.	Evaporation after removing Bismuth.	254
	Ammonia.	Fumes with Acetic Acid.	97
	Antimony, Arsenic, Tin.	Sulphuretted Hydrogen, etc.	254
	Arsenic.	Nascent Hydrogen and Nitrate of Silver.	171
Bismuthi Subnitras,	Carbonate.	Nitric Acid.	311
	Insoluble foreign salts.	Nitric Acid.	372
Bromum,	Chlorine (excess).	Ammonia and Carbonate of Barium.	266

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Bromum,	Iodine.	Gelatinized Starch.	266
Caffeina,	Mineral matter.	Incineration.	100
Calcii Bromidum,	Bromate.	Sulphuric Acid.	268
	Iodide.	Chlorine and mucilage of Starch.	271
	Sulphate.	Nitrate or Chloride of Barium.	307
	Chloride.	Nitrate of Silver, Carbonate of Ammonia, and Nitric Acid.	271
	Magnesium.	Phosphate of Sodium.	122
Calcii Carbonas Præcip.,	Magnesium.	Phosphate of Sodium.	122
	Aluminium, Iron, or Phosphate of Calcium.	Ammonic Hydrate.	371
Calcii Chloridum,	Aluminium, Iron, etc.	Ammonic Hydrate.	371
	Sulphate (of Calcium).	Chloride or Nitrate of Barium.	307
	Magnesium (more than trace).	Phosphate of Sodium.	122
Calcii Hypophosphis,	Insoluble Calcium Salts.	Solution in water.	370
	Soluble Phosphate.	Acetate of Lead.	211
	Sulphate.	Chloride or Nitrate of Barium.	307
	Magnesium.	Phosphate of Sodium.	122
Calcii Phosphas Præcip.,	Carbonate (of Calcium).	Solution in Acids.	311
	Aluminium.	Boiling Caustic Potash.*	137
Calx,	Excess of Carbonate.	Nitric Acid.	311
	Silica.	Nitric Acid.	372
Cambojia,	Starch.	Iodine.	271
	Bark, Sand, etc.	Microscope after exhaustion with Spt. and water.	403
Carbo Animalis Purificatus,	Earthy Salts.	Incineration with Mercuric Oxide.	100
	Phosphate (of Calcium).	Ammonia and Sulphate of Magnesium.	328
Carbonei Bisulphidum,	Sulphurous Acid.	Litmus-paper.	94
	Sulphuretted Hydrogen.	Acetate of Lead.	211
Cera Alba, Cera Flava,	Soap.	Hydrochloric Acid.	465
	Fats, Japan Wax, Resin.	Soda and Hydrochloric Acid.	465
	Paraffin.	Sulphuric Acid and dilution.	465
Cerii Oxalas,	Didymium.	Incineration.	226
	Aluminium.	Boiling in Caustic Potash, Chloride of Ammonium.	226
	Zinc.	Caustic Potash and Sulphide of Ammonium.	226
	Carbonate (of Cerium).	Hydrochloric Acid.	311
	Metallic impurities.	Sulphuretted Hydrogen.	218

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Cetaceum,	Soft Fats.	Melting-point.	526
Chinoidinum,	Alkaloidal Salts.	Alkali to hot solution.	388
	Mineral matter.	Incineration.	100
Chloral,	Acids.	Litmus.	94
	Hydrochloric Acid.	Nitrate of Silver.	264
	Mineral matter.	Incineration.	100
	Other organic impurity.	Sulphuric Acid.	445
	Alcoholate (of Chloral).	Chloroform.	445
	Alcoholate (of Chloral).	Boiling-point (above 97°).	525
	Alcoholate (of Chloral).	Formation of Iodoform.	429
Chloroformum Purificatum,	Acids.	Litmus.	94
	Chlorides.	Nitrate of Silver.	264
	Free Chlorine.	Iodide of Potassium.	271
	Aldehyd.	Solution of Potash.	430
	Hydrocarbons, etc.	Sulphuric Acid; odor on evaporation.	442
Chloroformum Venale,	Chlorides.	Nitrate of Silver.	264
	Much Hydrocarbons, etc.	Sulphuric Acid.	442
	Non-volatile matter.	Evaporation.	100
Chrysarobinum,	Mineral matter.	Incineration.	100
Cinchonidinæ Sulphas,	More than traces of Quinine or Quinidine.	Fluorescence of solution.	387
	Organic impurity.	Sulphuric Acid.	442
	Sulphate of Cinchonine.	Quantitative Analysis.	624
Cinchonina,	Quinine or Quinidine (much).	Fluorescence.	387
	Organic impurity.	Sulphuric Acid.	442
Coccus,	Insoluble matter.	Solution in cold water.	370
Codeina,	Morphine.	Nitric Acid.	381
Copaiba,	Fixed Oils.	Evaporation of volatile oil.	480
	Turpentine.	Odor when heated.	480
	Gurjun Balsam.	Oxidation.	480
Creasotum,	Carbolic Acid.	Albumen.	449
	Carbolic Acid.	Ferric Chloride.	449
	Carbolic Acid.	Glycerin.	449
	Carbolic Acid.	Dextro-rotation of polarized ray.	449
Creta Præparata,	Barium or Strontium.	Sulphate of Calcium.	254
	Magnesium.	Phosphate of Sodium.	122
	Iron.	Ferrocyanide of Potassium.	158
Cupri Acetas,	Lead or Iron.	Sulphuretted Hydrogen in alkaline solution.	189
	Alkalies or alkaline earths.	Evaporation after removing Copper.	189

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Cupri Sulphas,	Foreign metals.	Evaporation after removing Copper.	189
Elaterinum,	Alkaloids.	Tannic Acid; Salts of Platinum or Mercury.	
Fel Bovis Purificatum,	Mucus, crude Bile.	Incomplete solubility in spirit.	464
Ferri Carbonas Saccharatus,	Sulphate.	Chloride or Nitrate of Barium.	307
	General.	Quantitative Analysis.	577
Ferri Chloridum,	Zinc or Copper.	Ammonia, then Sulphuretted Hydrogen.	133
	Alkalies.	Evaporation and Incineration after adding Ammonia.	100
	Nitric Acid.	Sulphate of Iron and Sulphuric Acid.	286
	Ferrous Salt.	Ferrocyanide of Potassium.	158
	Oxychloride.	Boiling with water (insoluble).	370
Ferri Citras,	Fixed Alkalies.	Litmus to residue on incineration.	100
Ferri et Ammonii Citras,	Fixed Alkalies.	Litmus to residue on incineration.	100
Ferri et Ammonii Sulphas,	Aluminium.	Potassic Hydrate, then Chloride of Ammonium.	137
Ferri et Ammonii Tartras,	Fixed Alkalies.	Litmus to residue on incineration.	100
Ferri et Quininæ Citras,	Fixed Alkalies.	Litmus to residue on incineration.	100
	Ammonium Citrate.	Heating with Potash.	97
Ferri et Strychninæ Citras,	Fixed Alkalies.	Litmus to residue on incineration.	100
Ferri Hypophosphis,	Ferric Phosphate.	Solubility in Acetic Acid.	328
	Calcium.	Oxalate of Ammonium.	113
Ferri Iodidum Saccharatum,	Salts of Alkalies.	Incineration and digestion with water.	100
	Free Iodine.	Mucilage of Starch.	271
Ferri Lactas,	Sulphate, Citrate, Tartrate, etc.	Acetate of Lead.	211
Ferri Sulphas,	Copper, Ferric Salt.	Sulphuretted Hydrogen solution.	157 189
Ferrum Reductum,	Less than 80 per cent.	Quantitative Analysis.	592
Glycerinum,	Cane-sugar.	Sulphuric Acid.	454
	Sugars and Dextrin.	Ignition on sand-bath.	454
	Sugars.	Potassio-cupric Tartrate.	454
	Metallic Salts.	Ignition.	100
	Acrylic Acid.	Nitrate of Silver.	454
	Hydrochloric Acid.	Nitrate of Silver.	264
	Sulphuric Acid.	Chloride or Nitrate of Barium.	307
	Oxalic Acid.	Chloride of Calcium.	314
	Iron Salts.	Sulphide of Ammonium.	157

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Glycerinum,	Calcium Salts.	Oxalate of Ammonium.	113
Gossypium,	Acids or Alkalies.	Litmus.	94
Hydrargyri Chlor. Corros.,	Arsenic.	Nascent Hydrogen.	171
Hydrargyri Chlor. Mite,	Mercuric Chloride.	Sulphuretted Hydrogen.	199
	Fixed soluble impurities.	Residue on evaporating aqueous solution.	100
	Ammoniated Mercury.	Potash.	97
Hydrargyri Cyanidum,	Mercuric Chloride.	Iodide of Potassium.	201
Hydrargyri Iodidum Rubrum,	Chloride or soluble Iodide.	Nitrate of Silver.	264
Hydrargyri Iodidum Viride,	Mercuric Iodide.	Solution in Alcohol and evaporation.	193
Hydrargyri Oxidum Rubrum,	Mercuric Nitrate.	Strong heat.	200
Hydrargyri Subsulphas Flavus,	Mercurous Salt.	Solubility in Hydrochloric Acid.	197
Hydrargyri Sulphidum Rubrum,	Arsenic, Antimony.	Digestion with Potash and addition of HCl.	173
	Chromates, Iodides, or foreign Sulphides.	Acetate of Lead to Potash solution.	211
	Oxide of Mercury or Lead.	Digest with diluted HNO_3; pass Sulphuretted Hydrogen.	203
Hydrargyrum,	Foreign metals.	Hyposulphite of Sodium.	191
Hydrargyrum Ammoniatum,	Mercurous Salt.	Solubility in Hydrochloric Acid.	
	Carbonate.	Hydrochloric Acid.	311
	Lead.	Sulphuric Acid to acetic solution.	211
Hyoscyaminæ Sulphas,	Mineral matter.	Incineration.	100
Ichthyocolla,	Gelatin.	Solubility in water.	459
Iodoformum,	Alkali.	Litmus.	94
	Iodide.	Nitrate of Silver.	271
	Mineral matter.	Incineration.	100
Iodum,	Moisture.	Solubility in Chloroform.	269
	Chloride of Iodine.	Solubility in water.	269
	Cyanide of Iodine.	Formation of Prussian Blue.	270
	Chlorine or Bromine.	Nitrate of Silver.	270
Limonis Succus,	Deficiency of Citric Acid.	Sp. gravity and Quantitative Analysis.	322
	Foreign Acids.	General Analysis.	322
Linum,	Deficiency of Oil.	Extraction with Bisulphide of Carbon.	466
Liq. Ammonii Acetatis,	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Empyreumatic substances.	Odor when warmed, or Permanganate of Potash.	92

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Liq. Ammonii Acetatis,	Fixed saline matter.	Incineration.	100
Liquor Calcis,	Alkalies and alkaline Carbonates.	Precipitation by CO_2; test-papers.	94
Liq. Ferri Acetatis,	Zinc or Copper.	Excess of Ammonia and Sulphuretted Hydrogen.	133
	Fixed Alkalies.	Excess of Ammonia, and incineration.	157
	Ferrous Salt.	Ferricyanide of Potassium.	157
Liq. Ferri Chloridi,	Zinc or Copper.	Excess of Ammonia and Sulphuretted Hydrogen.	133
	Fixed Alkalies.	Excess of Ammonia, and incineration.	157
	Nitric Acid.	Sulphuric Acid and Ferrous Sulphate.	286
	Ferrous Salt.	Ferricyanide of Potassium.	157
	Oxychloride.	Solubility in water.	146
Liq. Ferri Citratis,	Ammonium Citrate.	Potash.	97
Liq. Ferri Subsulphatis,	Nitric Acid.	Sulphuric Acid and Ferrous Sulphate.	286
	Ferrous Salts.	Ferricyanide of Potassium.	157
Liq. Ferri Tersulphatis,	Nitric Acid.	Sulphuric Acid and Ferrous Sulphate.	286
	Ferrous Salts.	Ferricyanide of Potassium.	157
Liq. Hydrargyri Nitratis,	Mercurous Salt.	Hydrochloric Acid.	204
Liq. Pepsini,	Mucus.	Ammoniacal odor on keeping.	461
Liquor Potassæ,	Carbonate (of Potassium).	Hydrochloric or Acetic Acid.	311
	Alkaline earths.	Carbonate of Sodium to neutral solution.	106
	Sulphate.	Chloride or Nitrate of Barium.	307
	Chloride.	Nitrate of Silver.	264
Liq. Potassii Citratis,	(*Vide* Potassii Citras.)		
Liquor Sodæ,	Carbonate.	Hydrochloric or Acetic Acid.	311
	Alkaline earths.	Carbonate of Sodium to neutral solution.	106
	Sulphate.	Chloride or Nitrate of Barium.	307
	Chloride.	Nitrate of Silver.	264
Liq. Sodii Silicatis,	Much Alkali.	Quantitative Analysis.	560
Liq. Zinci Chloridi,	(*Vide* Zinci Chloridum.)		
Lithii Benzoas,	Salts of Alkalies.	Alcohol and Ether.	223

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Lithii Benzoas,	Salts of alkaline earths.	Oxalate of Ammonium.	113
	Metallic Salts.	Sulphuretted Hydrogen.	218
	Cinnamic Acid, etc.	(*Vide* Acidum Benzoicum.)	637
Lithii Bromidum,	Salts of Alkalies.	Alcohol and Ether.	223
	Salts of alkaline earths.	Oxalate of Ammonium.	113
	Metallic Salts.	Sulphuretted Hydrogen.	218
Lithii Carbonas, *Lithii Citras,* *Lithii Salicylas,*	(*Vide* Lithii Benzoas.)		223
Lupulinum,	Sand, etc.	Solubility in water.	370
Lycopodium,	Pollen, Starch.	Microscopical examination.	403
	Sand, or more than 5 per cent. of ash.	Incineration.	100
Magnesia, *Magnesia Ponderosa,*	Carbonate.	Dilute Sulphuric Acid.	118
	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Calcium.	Oxalate of Ammonium to acetic solution.	113
Magnesii Carbonas,	Aluminium or Calcium.	Carbonate and Chloride of Ammonium.	113
	Metals.	Sulphydrate of Ammonium and Ammonia.	137
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
Magnesii Citras Gran.,	Tartrate.	Acetate of Potassium and Acetic Acid.	319
Magnesii Sulphas,	Metallic Salts.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Alkaline earths.	Carbonate, Chloride, and Hydrate of Ammonium.	113
	Chloride.	Nitrate of Silver.	264
	Alkaline Sulphates.	Chloride of Barium, after removing Magnesia.	307
Magnesii Sulphis,	Sulphate of Magnesium.	Chloride of Barium.	307
Mangani Sulphas,	Iron.	Tannic Acid.	354
	Copper.	Sulphuretted Hydrogen.	218
	Alkalies or Magnesia.	Ignition after removing Manganese.	229
Manna,	Insoluble matter.	Digestion with Alcohol.	
	Deficiency of Mannite.	Quantitative Analysis.	415
Mel,	Chlorides.	Nitrate of Silver.	264
	Sulphates.	Chloride of Barium.	307
	Starch.	Iodine.	271
	Glucose, etc.	Mixture with water and Alcohol. Amount of ash on incineration.	414

Table of Tests—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Morphina,	Other Alkaloids.	Solubility in Sodic Hydrate.	
	Brucine, Strychnine, etc.	Sulphuric Acid, afterward Bichromate.	389
	Mineral matter.	Incineration.	100
Oleum Æthereum,	Acid (Sulpho-vinic).	Litmus.	94
Oleum Amygdalæ Amaræ,	Alcohol or Chloroform.	Distillation at 80° C.	446
	Nitrobenzol.	Nascent Hydrogen, and then Chlorate of Potassium.	417
Oleum Amygdalæ Expressum,	Foreign oils.	Sulphuric Acid.	466
Oleum Gaultheriæ,	Chloroform or Alcohol.	Distillation at 80° C.	446
	Oil of Sassafras.	Nitric Acid.	446
Oleum Lavandulæ Florum,	Alcohol.	Distillation at 80° C.	446
Oleum Olivæ,	Foreign oils.	General.	466
Oleum Sinapis Volatile,	Disulphide of Carbon.	Distillation at 50° C.	310
Oleum Theobromæ,	Paraffin, Wax,	Congelation-point after melting.	465
	Stearin, Tallow, etc.	Melting-point not above 15° C.	465
Olea Destillata,	General.	Solubility in Alcohol, sp. gravity, etc.	542
Opium,	Deficiency in Morphine.	Quantitative Analysis.	627
Pepsinum Saccharatum,	Mucus.	Turbidity of Hydrochloric Acid solution.	461
Petrolatum,	Fat or Resin.	Odor on ignition.	448
	Oils, Fats, or Resin.	Sulphuric Acid to its "soap."	448
	Other organic impurities.	Sulphuric Acid.	448
Phosphorus,	Arsenic.	Hydrosulphuric Acid to its Phosphoric Acid.	327
	Sulphur.	Chloride of Barium to its Phosphoric Acid.	327
Physostigminæ Salicylas,	Mineral matter.	Incineration.	100
Picrotoxinum,	Mineral matter.	Incineration.	100
	Alkaloids.	Precipitated by Tannic Acid, Platinum Salts, etc.	
Pilocarpinæ Hydrochloras,	Mineral matter.	Incineration.	100
Piperina,	Mineral matter.	Incineration.	100
Plumbi Acetas,	Zinc, Alkalies, or alkaline earths.	Precipitation by SH_2, and evaporation of filtrate.	189
	Copper.	Excess of Ammonia.	189
Plumbi Carbonas,	Zinc.	Sulphydrate of Ammonium after removing Lead.	133

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Plumbi Carbonas,	Calcium (chalk).	Oxalate of Ammonium after removing Lead.	113
	Sulphate of Barium or Lead.	Insolubility in Acetic Acid.	102 211
	Silicates.	Insolubility in Acetic Acid.	351
	Alkaline Salts.	Evaporation after removing Lead.	69
Plumbi Iodidum,	Chromate (of Lead).	Solubility in Chloride of Ammonium.	211
	Zinc, etc.	Evaporation after removing Lead.	69
Plumbi Nitras.	Zinc, etc.	Evaporation after removing Lead.	69
	Copper.	Excess of Ammonia.	189
Plumbi Oxidum,	Carbonate.	Dilute Acids.	311
	Zinc, etc.	Evaporation after removing Lead.	69
Potassa,	Organic matter.	Color of solution, and Permanganate of Potash.	92
	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Carbonate.	Effervescence with acids.	311
	Silica.	Solubility in Alcohol.	66
Potassa cum Calce,	Silica.	Solubility in Hydrochloric Acid.	351
Potassa Sulphurata,	Deficiency of Sulphide.	Sulphuretted Hydrogen.	68
Potassii Acetas,	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Silica.	Evap'n of acid solution, insolubility of residue.	351
	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Alkaline earths.	Carbonate of Sodium.	106
	Carbonate.	Effervescence with Acetic Acid.	311
	Organic impurities.	Sulphuric Acid.	297 320
Potassii Bicarbonas,	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Carbonate.	Chloride of Barium in the cold.	364
Potassii Bichromas,	Sulphate.	Chloride of Barium.	307
Potassii Bitartras,	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	More than 6 per cent. of Tartrate of Calcium.	Quantitative Analysis. " "	316 561
Potassii Bromidum,	Bromate.	Sulphuric Acid.	268
	Iodide.	Chlorine and mucilage of Starch.	271

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Potassii Bromidum,	Sulphate.	Chloride of Barium.	307
	More than 3 per cent. of Chloride.	Quantitative Analysis.	569
Potassii Carbonas,	Silica, etc.	Insolubility of residue on evaporation of acid solution.	351
	Alkaline earths.	Carbonate of Sodium.	106
	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
Potassii Chloras,	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Calcium.	Oxalate of Ammonium.	113
Potassii Citras,	Carbonate.	Effervescence with acids.	311
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Tartrate.	Acetic Acid.	319
Potassii Cyanidum,	Carbonate.	Effervescence with Acids.	311
Potassii et Sodii Tartras,	Calcium.	Oxalate of Ammonium.	113
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
Potassii Ferrocyanidum,	Carbonate.	Effervescence with Acids.	311
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
Potassii Hypophosphis,	Carbonate.	Effervescence with Acids.	311
	Sulphate.	Chloride of Barium.	307
	Phosphate.	Magnesia mixture.	328
	Calcium.	Oxalate of Ammonium.	113
Potassii Iodidum,	Iodate.	Mucilage of Starch and Tartaric Acid.	75
	Chloride or Bromide.	Ammonia, Nitrate of Silver, and Nitric Acid.	271
	Sulphate.	Chloride of Barium.	307
Potassii Nitras,	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Alkaline earths.	Carbonate of Ammonium.	102 113 119
	Sulphate.	Chloride of Barium.	307
	Chloride (of Sodium).	Nitrate of Silver.	264
Potassii Permanganas,	Nitrate.	Sulphuric Acid and Ferrous Sulphate to decolorized solution.	286
	Chloride.	Nitrate of Silver to decolorized solution.	264
	Sulphate.	Nitrate of Barium after removing Manganese by Ammonia.	307
Potassii Sulphas,	Alkaline earths.	Carbonate or Phosphate of Ammonium.	122
	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Chloride.	Nitrate of Silver.	264
Potassii Sulphis,	Sulphate.	Chloride of Barium.	307

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Potassii Tartras,	Calcium.	Oxalate of Ammonium.	113
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
Quinidinæ Sulphas,	Organic impurities.	Sulphuric Acid.	386
	Morphine.	Nitric Acid.	381
	Cinchonine, Quinine, or Cinchonidine.	Iodide of Potassium and Ammonic Hydrate.	387
Quinina,	Organic impurities.	Sulphuric Acid.	386
	Cinchonine, Cinchonidine, or Quinidine.	Sulphate of Ammonium and Ammonia.	624
Quininæ Bisulphas,	Organic impurities.	Sulphuric Acid.	386
	Free water.	Drying upon water-bath.	624
	Sulphates of Quinidine, Cinchonidine, or Cinchonine.	Ammonia, as for Quinine.	624
Quininæ Hydrobromas,	Organic impurities.	Sulphuric Acid.	386
	Free water.	Drying upon water-bath.	385
	Sulphate.	Chloride of Barium.	307
	Barium.	Sulphuric Acid.	102
	Cinchonine, etc.	Ammonia, as for Quinine.	624
Quininæ Hydrochloras,	Organic impurities.	Sulphuric Acid.	386
	Barium.	Sulphuric Acid.	102
	Sulphate.	Chloride of Barium.	307
Quininæ Sulphas,	Organic impurities.	Sulphuric Acid.	386
	Ammonia (Sulphate).	Boiling with milk of lime.	97
	Free water.	Drying on water-bath.	624
	Cinchonine Sulphate, etc.	Ammonium Hydrate.	624
Quininæ Valerianas,	Organic impurities.	Sulphuric Acid.	386
	Sulphate.	Chloride of Barium.	307
Rheum,	Turmeric.	Boracic Acid.	331
Saccharum,	Insoluble salts, etc.	Aqueous or alcoholic solution on standing.	
	Grape-Sugar or Inverted Sugar.	Nitrate of Silver and Ammonic Hydrate.	412
Saccharum Lactis,	Cane-Sugar.	Sulphuric Acid.	413
Salicinum,	Mineral matter.	Incineration.	100
Santoninum,	Mineral matter.	Incineration.	100
Sapo,	More than 34 per cent. of water.	Drying at 110° C.	610
	Animal Fats.	Gelatinization of 4 per cent. alcoholic solution.	463
	Carbonate of Sodium.	Solubility in alcohol.	463
	Silica and insoluble matter.	Solubility in water.	463
	Metals.	Sulphuretted Hydrogen.	218
Sapo Viridis,	More than 4 per cent. of water.	Drying at 100° C.	610
	Free Fats.	Digestion of dried soap in Benzol.	463

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Sapo Viridis,	Insoluble Carbonates.	Dilute Acids to residue from alcohol and water.	311
	Starch.	Iodine to residue from alcohol and water.	271
Scammonium,	Chalk.	Effervescence with Acids.	311
	Starch.	Iodine.	271
Scammonii Resina,	Resin of Guaiacum.	Inner surface of potato-paring.	421
	Resin of Jalap.	Insolubility in Ether.	421
Soda,	Organic matter.	Color of aqueous solution: Sulphuric Acid.	
	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Carbonate.	Effervescence with Acids.	311
	Silica or Carbonate.	Solubility in Alcohol.	67
Sodii Acetas,	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Silica.	Insolubility of residue on evaporating acid solution.	351
	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Alkaline earths.	Carbonate of Sodium.	106
	Carbonate.	Effervescence with Acids.	311
	Organic impurities.	Sulphuric Acid.	297 320
Sodii Arsenias,	Arsenite.	Sulphuretted Hydrogen water.	172
	Excess or deficiency of water of crystallization.	Quantitative Analysis.	610
Sodii Benzoas,	(*Vide* Acidum Benzoicum.)		637
Sodii Bicarbonas,	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Ammonium Salts.	Boiling with solution of Soda.	97
	Carbonate.	Chloride of Barium in the cold, and Quantitative Analysis.	364 560
Sodii Bisulphis,	Sulphate.	Chloride of Barium.	307
Sodii Boras,	Carbonate.	Effervescence with Acids.	311
	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
	Alkaline earths.	Carbonate of Sodium.	106
	Metals.	Hydrosulphuric Acid.	218
Sodii Bromidum,	Bromate.	Sulphuric Acid.	268
	Iodide.	Chlorine-water and mucilage of Starch.	271
	Sulphate.	Chloride of Barium.	307
	More than 3 per cent. of Chloride.	Quantitative Analysis.	570
Sodii Carbonas,	Chloride.	Nitrate of Silver.	264

TABLE OF TESTS—*Continued.*

Name of Preparation.	Impurities.	Tests.	Page.
Sodii Carbonas.	Sulphate.	Chloride of Barium.	307
	Metals.	Hydrosulphuric Acid.	218
	Alumina.	Ammonia and Chloride of Ammonium.	137
Sodii Chloras,	Potassium.	Bitartrate of Sodium.	78
	Calcium.	Oxalate of Ammonium.	113
	Chloride.	Nitrate of Silver.	264
	Sulphate.	Chloride of Barium.	307
Sodii Chloridum,	Metals.	Hydrosulphuric Acid or Sulphide of Ammonium.	218
	Alkaline earths.	Carbonate of Sodium.	103
	Sulphate.	Chloride of Barium.	307
	Iodide or Bromide.	Chlorine-water and Starch to residue on evaporating alcoholic solution.	268
Sodii Hypophosphis,	Calcium.	Oxalate of Ammonium.	113
	Potassium.	Bitartrate of Sodium.	78
	Carbonate.	Effervescence with Acids.	311
	Sulphate.	Chloride of Barium.	307
	Phosphate.	Ammonia and Sulphate of Magnesium.	328
Sodii Hyposulphis,	Sulphate.	Chloride of Barium.	307
	Carbonate.	Effervescence with Acids.	311
Sodii Iodidum,	Iodate.	Mucilage of Starch and Tartaric Acid.	75
	Sulphate.	Chloride of Barium.	307
	Chloride or Bromide.	Ammonia, Nitrate of Silver, and Nitric Acid.	271
Sodii Nitras,	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
	Alkaline earths.	Carbonate of Ammonium.	113
	Potassium.	Bitartrate of Sodium.	78
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Iodide.	Chlorine-water and Mucilage of Starch.	271
Sodii Phosphas,	Carbonate.	Effervescence with Acids.	311
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
Sodii Pyrophosphas,	Carbonate.	Effervescence with Acids.	311
	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
	Metals.	Sulphuretted Hydrogen or Sulphide of Ammonium.	218
Sodii Salicylas,	Carbonate.	Effervescence with Acids.	311
	Sulphate.	Chloride of Barium.	307
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	Sulphate.	Chloride of Barium.	307
	Chloride.	Nitrate of Silver.	264
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Zinci Bromidum,	Lead or Copper.	Hydrosulphuric Acid.	218
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Name of Preparation.	Impurities.	Tests.	Page.
Zinci Bromidum,	Alkalies or alkaline earths.	Evaporation and ignition, after removing Zinc.	133
Zinci Carbonas Præcipitatus,	Lead or Copper.	Hydrosulphuric Acid.	218
	Iron, Aluminium, or alkaline earths.	Carbonate of Ammonium in excess.	133
	Salts of Alkalies or alkaline earths.	Evaporation and ignition, after removing Zinc.	133
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Zinci Phosphidum,	Lead or Copper.	Hydrosulphuric Acid.	218
Zinci Sulphas,	Chloride.	Nitrate of Silver.	264
	Same as other Zinc Salts.		
Zinci Valerianas,	Alkalies or alkaline earths.	Evaporation and ignition, after removing Zinc.	133
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SATURATION TABLES.

Equivalent Weights of Citric Acid, Tartaric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium, Bicarbonate of Sodium, Carbonate of Ammonium, and Carbonate of Magnesium, repeated (in **black**) for 20 parts of each, and incidentally (in Roman) for other proportions. (Exact to two places of decimals.)

Citric Acid ($H_3C_6H_5O_7.H_2O$) ÷ 3 × 2 = 140	**20.00**	18.66	**16.96**	**14.00**	**9.78**	**16.66**	**23.72**	**29.31**
Tartaric Acid $H_2C_4H_4O_6$ = 150	21.43	**20.00**	**18.26**	**15.00**	**10.49**	**17.85**	**25.42**	**31.41**
Carbonate of Potassium K_2CO_3 + 16% Aq. = 164.285	**23.47**	**21.90**	**20.00**	16.43	11.48	19.52	27.87	34.40
Bicarbonate of Potassium 2($KHCO_3$) = 200	**28.57**	**26.66**	24.34	**20.00**	13.98	23.81	33.89	41.90
Carbonate of Sodium $Na_2CO_3,10H_2O$ = 286	**40.08**	**38.13**	34.81	28.60	**20.00**	34.04	48.47	59.98
Bicarbonate of Sodium 2($NaHCO_3$) = 168	**24.00**	**22.40**	20.45	16.80	11.74	**20.00**	28.47	35.18
Carbonate of Ammonium ($N_4H_{16}C_3O_8$) ÷ 2 = 118	**16.85**	**15.73**	14.36	11.80	8.25	14.04	**20.00**	24.71
Carb. of Magnes. (($MgCO_3)_3,Mg2HO,4H_2O$) ÷ 4 = 95.5	**13.64**	**12.73**	11.62	9.55	6.68	11.37	16.18	**20.00**

The amount of acid given in any column will saturate the amount of carbonate in the same column, and *vice versâ*.

The amounts of carbonate in any column are equal to each other in chemical power.

Lemon-juice (sp. gr. 1.039) contains, on an average, 7 per cent. by weight of citric acid.

The same Table in Round Numbers, for Purposes of Prescribing and Dispensing.

(The old names in Latin.)

Citric Acid	**20**	19	**17**	**14**	**10**	**17**	**24**	**30**
Tartaric Acid	22	**20**	**18**	**15**	**11**	**18**	**26**	**32**
Carbonate of Potassium (Potassæ Carbonas)	**24**	**22**	**20**	16	12	20	28	35
Bicarbonate of Potassium (Potassæ Bicarbonas)	**29**	**27**	24	**20**	14	24	34	42
Carbonate of Sodium (cryst.) (Sodæ Carbonas)	**40**	**38**	35	28	**20**	34	49	60
Bicarbonate of Sodium (Sodæ Bicarbonas)	**24**	**22**	20	17	12	**20**	29	36
Carbonate of Ammonium (Ammoniæ Carbonas)	**17**	**16**	14	12	8	14	**20**	25
Carbonate of Magnesium (Magnesiæ Carbonas)	**13**	**13**	11	9	7	11	16	**20**

The Table is read thus: 20 grains of Citric Acid will saturate 29 grains of Bicarbonate of Potassium; 20 grains of Bicarbonate of Sodium will saturate, or be saturated by, 18 grains of Tartaric Acid; 11 grains of Tartaric Acid = 8 grains of Carbonate of Ammonium; 20 grains of Bicarbonate of Sodium are equivalent to, or will do as much work as, 34 grains of Carbonate of Sodium; 14 grains of Citric Acid are as strong as 15 of Tartaric Acid. It is occasionally convenient to double the numbers, halve them, or take some other proportion; also to employ them in weights other than grains.

Lemon-juice contains, on an average, 32½ grains of citric acid in 1 fluidounce, or 4 grains per fluidrachm.

The Proportion by Weight of Absolute or Real Alcohol (C_2H_5HO) *in 100 Parts of Spirits of Different Specific Gravities* (*Fownes*).

Sp. gr. at 60° (15°.5 C.).	Percentage of real alcohol.	Sp. gr. at 60° (15°.5 C.).	Percentage of real alcohol.	Sp. gr. at 60° (15°.5 C.).	Percentage of real alcohol.
0.9991	0.5	0.9511	34	0.8769	68
0.9981	1	0.9490	35	0.8745	69
0.9965	2	0.9470	36	0.8721	70
0.9947	3	0.9452	37	0.8696	71
0.9930	4	0.9434	38	0.8672	72
0.9914	5	0.9416	39	0.8649	73
0.9898	6	0.9396	40	0.8625	74
0.9884	7	0.9376	41	0.8603	75
0.9869	8	0.9356	42	0.8581	76
0.9855	9	0.9335	43	0.8557	77
0.9841	10	0.9314	44	0.8533	78
0.9828	11	0.9292	45	0.8508	79
0.9815	12	0.9270	46	0.8483	80
0.9802	13	0.9249	47	0.8459	81
0.9789	14	0.9228	48	0.8434	82
0.9778	15	0.9206	49	0.8408	83
0.9766	16	0.9184	50	0.8382	84
0.9753	17	0.9160	51	0.8357	85
0.9741	18	0.9135	52	0.8331	86
0.9728	19	0.9113	53	0.8305	87
0.9716	20	0.9090	54	0.8279	88
0.9704	21	0.9069	55	0.8254	89
0.9691	22	0.9047	56	0.8228	90
0.9678	23	0.9025	57	0.8199	91
0.9665	24	0.9001	58	0.8172	92
0.9652	25	0.8979	59	0.8145	93
0.9638	26	0.8956	60	0.8118	94
0.9623	27	0.8932	61	0.8089	95
0.9609	28	0.8908	62	0.8061	96
0.9593	29	0.8886	63	0.8031	97
0.9578	30	0.8863	64	0.8001	98
0.9560	31	0.8840	65	0.7969	99
0.9544	32	0.8816	66	0.7938	100
0.9528	33	0.8793	67		

THE ELEMENTS.

	Symbols and atomic value.	Atomic weight.
Aluminium (Al_2^{VI})	Al^{I}	27
Antimony (Sb^{III})	Sb^{V}	120
Arsenicum (As^{III})	As^{V}	74.9
Barium	Ba^{II}	136.8
Beryllium (Glucinum)	Be^{II}	9
Bismuth (Bi^{III})	Bi^{V}	210
Boron	B^{III}	11
Bromine ($^{79.75,\ \text{Stas}}$)	Br^{I}	79.8
Cadmium	Cd^{III}	111.8
Cæsium	Cs^{I}	132.6
Calcium	Ca^{II}	40
Carbon (C^{II})	C^{IV}	12
Cerium (Ce^{III}) ($^{138,\ \text{Mendelejeff}}$)	Ce^{VI}	141
Chlorine ($^{35.368,\ \text{Stas}}$)	Cl^{I}	35.4
Chromium (Cr_2^{VI})	Cr^{VI}	52.4
Cobalt (Co^{II})	Co^{VI}	58.9
Copper	Cu^{II}	63.2
Davyum ?		
Decipium ?	Dp^{II}	
Didymium ($^{138,\ \text{Mendelejeff}}$)	D^{II}	144.6
Erbium ? ($^{171,\ \text{Mendelejeff}}$)	Eb^{II}	165.9
Fluorine	F^{I}	19
Gallium	Ga^{IV}	68.8
Glucinum. See Beryllium.		
Gold (Au^{I})	Au^{III}	196.2
Hydrogen	H^{I}	1
Ilmenium ?	Il^{V}	
Indium ($^{113,\ \text{Mendelejeff}}$)	In^{VI}	56.7
Iodine ($^{126.533,\ \text{Stas}}$)	I^{I}	126.6
Iridium	Ir^{IV}	192.7
Iron (Fe^{II} & Fe_2^{VI})	Fe^{VI}	55.9
Lanthanum ($^{138,\ \text{Mendelejeff}}$)	La^{II}	138.5
Lavoisium ?		
Lead ($^{II}Pb^{II}$)	Pb^{IV}	206.5
Lithium ($^{7.004,\ \text{Stas}}$)	L^{I}	7
Magnesium	Mg^{II}	24
Manganese (Mn^{II} & Mn^{IV})	Mn^{VI}	54
Mercury	Hg^{II}	199.7
Molybdenum	Mo^{VI}	95.5
Mosandrum.		
Neptunium	Np^{V}	

	Symbols and atomic value.	Atomic weight.
Nickel (Ni^{II})	Ni^{VI}	58
Niobium	Nb^{V}	94
Nitrogen (N^{I} & N^{III}) ($^{\text{14.009, Stas}}$)	N^{V}	14
Norwegium.		
Osmium	Os^{IV}	99.5
Oxygen ($^{\text{15.96, Stas}}$)	O^{II}	16
Palladium	Pd^{IV}	105.7
Philippium ?	Pp^{II}	
Phosphorus (P^{III})	P^{V}	31
Platinum ($^{\text{197.88, Andrews}}$)	Pt^{IV}	194.4
Potassium ($^{\text{39.04, Stas}}$)	K^{I}	39
Rhodium	Rh^{IV}	104.1
Rubidium	Rb^{I}	85.3
Ruthenium	Ru^{IV}	104.2
Scandium.		
Selenium or Selenion	Se^{VI}	78.8
Silicon	Si^{IV}	28
Silver ($^{\text{107.66, Stas}}$)	Ag^{I}	107.7
Sodium ($^{\text{22.98, Stas}}$)	Na^{I}	23
Strontium	Sr^{II}	87.4
Sulphur (S^{II} & S^{IV})	S^{VI}	32
Tantalum	Ta^{V}	182
Tellurium	Te^{VI}	128
Terbium ?	Tb^{II}	
Thallium ($^{\text{203, Crookes}}$)	Tl^{III}	203.7
Thorinum or Thorium	Th^{II}	233
Tin (Sn^{II})	Sn^{IV}	117.7
Titanium	Ti^{IV}	48
Tungsten	W^{VI}	183.6
Uralium ($^{\text{187.25, Guyard}}$)		
Uranium ($^{\text{240, Mendelejeff}}$)	U^{VI}	238.5
Vanadium	V^{V}	51.3
Ytterbium ?	Yb	172.7
Yttrium ($^{\text{90, Mendelejeff}}$)	Y^{II}	89.8
Zinc	Zn^{II}	64.9
Zirconium	Zi^{IV}	90

The *quantivalence* or atomic value of some elements is, apparently, variable; in the above Table the full coefficients are given in the column of symbols, other common values in parentheses.

Atomic weights are sometimes obscurely termed *equivalents*.

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